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CALORIMETRY, AND THE DETERMINATION OF THE CALORIFIC VALUE OF PHILIPPINE AND OTHER COALS FROM THE RESULTS OF PROXIMATE ANALYSIS.

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Many engineers are accustomed to judge of the steaming quality of coal from its specified heating value¹ rather than from the analysis of the fuel. To determine this a steaming test is not satisfactory, because different furnaces give different values and the personal equation of firing and manipulation enter to a large degree into the results. Steaming tests are useful only for comparative purposes and then only when they are carried out in identical apparatus and under like conditions.

The only absolutely reliable means of determining the heating value of a coal is by the use of a standard calorimeter which records accurately.

There are many kinds of calorimeters² of varying accuracy, some of which show discrepancies of as much as 15 per cent and are seldom if ever used. In general, the large apparatus is to be condemned, because it is impossible to detect the errors which creep in and to make allowance for them. This is not the place to describe the difficulties and defects connected with these calorimeters. In all cases the

¹The heating value of a coal is expressed in calories. A calorie is the amount of heat necessary to raise the temperature of 1 gram of water 1° C. The "pound calorie" is sometimes used by English writers; it is the amount of heat necessary to raise the temperature of 1 pound of water 1° C. The figures would be the same in either case, for when the heating value of a coal is given in calories it means that 1 gram of coal will heat the given number of grams of water 1° C. or that 1 pound of coal will heat the given number of pounds of water 1° C. One British thermal unit is the heat necessary to raise 1 pound of water 1° F., therefore, 1 calorie=9/5 B. T. U.

the end of this article.

²A bibliography of the literature of calorimeters, arranged alphabetically, is given at the end of this article.

burning takes place in pure oxygen. In all older calorimeters this occurs slowly under atmospheric pressure, while in a number of the more recent ones the explosion method is used; that is, the combustion occurs under a pressure of fifteen to twenty-five atmospheres. Another method used in some of the calorimeters is to effect combustion with combined oxygen. The explosion method is the one used in the Berthelot³ bomb and has the advantage over most of the other forms of apparatus in that perfect combustion is attained.⁴ In 1892, Mahler⁵ employed an enameled bomb and obtained results as satisfactory as with the platinum bomb of Berthelot, while the cost of the apparatus is much less. In 1849, Hempel⁶ introduced the idea of pressing the wire into the coal briquette for electrical incineration and in 1897 Kröker⁷ added to the bomb a head which was fitted with two gas-tight valves, which greatly facilitates the determination of the products of combustion. These points are all included in the Berthelot-Mahler⁸ bomb calorimeter which

³ See bibliography.

⁴ Fries, J. A. (*Journ. Am. Chem. Soc.* (1909), **31**, 272), using an Atwood bomb (which is a modification of that of Berthelot) with a modified top has shown that the determination of carbon by means of it "is absolutely reliable and gives very accurate results."

⁵ Mahler, P. *Ztschr. f. angew. Chem.* (1892), **5**, 491; (1898), **11**, 865.

⁶ Hempel, W. *Ibid.* (1892), **5**, 389; Langbein, H. *Ibid.* (1896), **9**, 488.

⁷ Kröker. *Ibid.* (1898), **11**, 865.

⁸ Calorimeter nach Berthelot-Mahler mit geänderter Einrichtung der Verbrennungsbombe (nach dem System von Dr. K. Kröker). Verfertiger, Julius Peters, Berlin, N. W., Thurmstr. 4. This is an apparatus in which the combustibles are burned in compressed oxygen in a vessel, called a "bomb," surrounded by a large quantity of water, and the products of combustion cooled by the water until the temperature is reduced to that of the water. Any water formed by the combustion is condensed, and its latent heat is also given up to the calorimeter. Corrections are made on the end temperature for the water value of the apparatus, for radiation and for the heat of formation of the products of combustion, including the water formed, and the difference determined between this result and the initial temperature. The increase in temperature is a measure of the heat-producing power of the coal. The calorific value is the product of the units of water by the degrees raised; that is, the heat produced by the burning of a unit weight of coal under these conditions.

The most troublesome source of error in careful calorimetric work is the loss or gain of heat by the calorimeter from its surroundings. Unavoidable irregularities in the conditions make this correction variable and its determination somewhat uncertain. Many methods of making it have been proposed. In the experiments given in this paper this loss, which is mostly due to radiation, was in the majority of cases taken into consideration according to the Regnault-Stohmann-Pfaundler formula (Stohmann, *Journ. f. prakt. Chem.* (1889), N. F. **39**, 517 *et seq.*), that is:

$$\text{The correction} = \frac{v-v'}{\tau'-\tau} \left(\frac{t_2-t_1}{9} + \frac{t_1+t_n}{2} + \sum_{1}^{n-1} (t) - n\tau \right) - (n-1) v \text{ where,}$$

v = the mean temperature difference of the preliminary period.

τ = the mean of the temperature readings of the preliminary period.

$t_1, t_2 \dots t_n$ = the temperature readings of the combustion period.

v' = the mean temperature difference of the period after combustion.

τ' = the mean of the temperature readings of the period after combustion.

n = the number of the temperature readings of the combustion period.

was used in my tests. This apparatus is generally accepted as being the most accurate.⁹ While accurate, it is nevertheless expensive and requires an elaborate equipment and a skill in manipulation which prevents as wide a usage as it deserves. A great many attempts have been made to find a substitute for this apparatus as is shown by the references given at the end of this paper; however, few of these other types give the calorific value more accurately than the result as calculated from easily obtained data. When the necessary apparatus for the direct determination of the heating power is not at hand, it is an important feature to have some means of approximately estimating the calorific value and it is one object of this paper to indicate a method for the calculation of this value for Philippine coal from the results of the proximate analysis. It is hoped that this calculation will fulfill the essential requirements for commercial purposes.

Owing to the recent revival of interest in Philippine coal, we now make many more analyses than formerly. It is not always convenient to undertake calorific determinations of all of these, but I have direct data in sufficient quantity to correlate a formula which will give a result approximately equal to that obtained with the calorimeter.

Many attempts have been made to develop a reliable formula for calculating the heating power from analytical data. That first proposed was by Dulong for the calculation of the heat of combustion from the results of ultimate analysis, and is as follows:

$$\text{Calorific power} = \frac{1}{100} \left[8080C + 34500 \left(H - \frac{O}{8} \right) \right]$$

Others who have contributed to the development of this line of work by furnishing data, suggesting formulæ or modifications of that given above are Gmelin, v. Jüptner, Cornut, Ser, Kern,¹⁰ Scheurer-Kestner, Meunier-Dollfus, Mahler, Bunte, etc. The calorific work done by Scheurer-Kestner and Meunier-

⁸ continued The results obtained by this formula agree very well with those from the empirical formula, which is a correction in calories of two-thirds of the difference between the highest temperature and that of the room, multiplied by four times the duration of the combustion in minutes; this correction was used in some cases. The temperature difference was determined by the use of a Beckmann thermometer.

Detailed directions for the manipulation of a bomb calorimeter in heat determinations, for the determination of the water value of the apparatus, the calculation of the results, etc., may be found, in the publications of Stohman, F., Kleber, Cl., and Langbein, H. *Journ. f. prakt. Chem.* (1889), N. F. **39**, 503; Atwood, W. O. and Snell, J. F. *Journ. Am. Chem. Soc.* (1903), **25**, 659, and also in many text-books.

⁹ Braume, J. S. S., and Cowan, W. A. *Journ. Soc. Chem. Ind.* (1903), **22**, 1232 and Gray, Tho. and Robertson, J. G. *Ibid.* (1904), **23**, 704 have made comparative studies of different types of calorimeters and agree that reliable results can be obtained only with some form of bomb calorimeter.

¹⁰ Liebig's process for the estimation of carbon and hydrogen in coals is discussed and the calorific value is calculated by use of the formula $8080C + 34,460H$. Kern, S. *Chem. News* (1876), **34**, 233.

Dollfus (1868-1875)¹¹ has long been considered the most reliable ever accomplished on European coal and has done much to further the determination of the heating power of coal and the substantiation of Dulong's formula. Beginning in 1885¹² these authors continued their earlier investigations and made a number of determinations in order to fix a fair average for all coals. They found the heating power of many coals to be greater than that calculated from the elements; the Russian coal gave results which were very much nearer, in fact, fell slightly below the calculated value; therefore, indicating that the calculated value was a fair approximation to the truth. Mahler¹³ has also done much careful work on European coal. He modified Dulong's formula by using the value 8140 for the heating power of carbon as determined by Berthelot and Petit¹⁴ instead of 8080 as determined by Favre and Silbermann¹⁵ and also so as to take into account the nitrogen content as follows:

$$\begin{aligned}\text{Calorific value} &= \frac{1}{100} \left[8140C + 34500 \left(H - \frac{(O+N)-1}{8} \right) \right] \\ &= \frac{1}{100} [8140C + 34500H - 4312.5((O+N)-1)]\end{aligned}$$

Mahler emphasized the fact that Dulong's formula generally gave results which were below the actual, corroborating the observations of Scheurer-Kestner and Meunier-Dollfus, and proposed the adoption of the formula modified to read:

$$\text{Calorific value} = \frac{8140C - 34500H - 3000(O-N)}{100}$$

The application of this to a large number of coals gave variations of about the same magnitude from the actual value as that of Dulong, but in the opposite direction.

Dulong's formula has stood the test through many years of discussion and suggested substitutions. The formula has no scientific value, but in 1891, Bunte,¹⁶ as the result of a series of investigations in Munich, showed it to be sufficiently accurate for all practical purposes; and in 1899 the report of the Committee on Coal Analysis¹⁷ appointed by the American Chemical Society gave it in the following form as the most reliable formula for the calculation of the heating effect of a coal burned to liquid water:

$$\text{"Calorific power} = 8080C + 34,460(H - \frac{1}{8}O) + 2250S"$$

¹¹ Scheurer-Kestner, A., and Meunier C. *Compt. rend. Acad. sci.* (1868), **66**, 1220; **67**, 659, 1002; (1869), **68**, 608; **69**, 412; (1871), **73**, 1061; (1873), **77**, 1385; *Ann. chim. et phys.* (1874), V, **2**, 325; *Bull. Soc. chim. Paris* (1874), n. s. II, **21**, 402. Scheurer-Kestner, A. *Compt. rend. Acad. sci.* (1868), **66**, 1047.

¹² Scheurer-Kestner, A., and Meunier-Dollfus, C. *Compt. rend. Acad. sci.* (1885), **100**, 908; *Ann. chim. et phys.* (1886), VI, **8**, 267.

¹³ Mahler, P. *Bull. Soc. encourag. ind. nat.* (1892), **91**, 358.

¹⁴ *Ann. chim. et phys.* (1889), VI, **18**, 80.

¹⁵ *Ibid.* (1852), III, **34**, 403.

¹⁶ *Journ. f. Gasbeleuchtung* (1891), **34**, 21 and 41.

¹⁷ *Journ. Am. Chem. Soc.* (1899), **21**, 1130.

The literature is full of material showing an agreement within 2 or 3 per cent between results obtained by direct determination and those calculated from elementary analyses.¹⁸ Lord and Haas¹⁹ have shown from their work that the results on American coals "if calculated from the ultimate analysis, might be expected to lie within two per cent of the calorific value" and the work of the Coal Testing Plant²⁰ at St. Louis has shown a similarly close agreement. However, all of these formulæ have the disadvantage that elementary analysis is too tedious for ordinary technical work. At the time these were originally proposed, it was much easier to make an elementary analysis, in point of time at least, than to make a determination of the heating power. To-day it is simpler to determine at once calorimetrically the heating power of the material than to carry out an elementary analysis.

The prediction of the heating power of a coal from the results of a proximate analysis was suggested by Kent²¹ in 1892.

He writes, "Mahler's results group themselves very closely around the average curve of the diagram, indicating therefore that there is a law of relation between the composition of the coal as determined by proximate analysis and the heating value. Knowing, therefore, the percentage of fixed carbon in the dry coal free from ash, we may in the case of all coals containing over 58 per cent of fixed carbon, predict their heating value within a limit of error of about 3 per cent."

A formula for the derivation of the calorific power from the proximate analysis was first proposed by Goutal²² in 1896. Later De Paepe²³ applied it to a wider range of coals and suggested some modifications for the values first proposed. Since then Goutal has extended his investigations to more than six hundred anthracitic and bituminous coals and finds²⁴ that the calorific value can be calculated with sufficient accuracy for industrial purposes.

Such a formula is only an approximation. It would be impossible to derive an absolutely correct formula from analyses made by an entirely empirical method, of a substance so complex and varied as coal. However, it has often been recorded²⁵ that the results obtained by calculation

¹⁸ Alix, J., and Bay, I. *Compt. rend. Acad. sci.* (1904), **139**, 215 have pointed out that nearly all coals contain more or less calcium carbonate, and in the ultimate analysis the carbon dioxide from this is also calculated to carbon. This may be a source of variation.

¹⁹ *Trans. Am. Inst. Min. Eng.* (1897), **17**, 268.

²⁰ *Prof. Papers* **48**, *U. S. Geol. Surv.* (1906), **1**, 174.

²¹ Kent, W. *Mineral Ind.* (1892), **1**, 105.

²² *Ann. chim. anal.* (1896), **1**, 169; *Rev. d. chim. ind.*, (1896), **7**, 65.

²³ De Paepe, D. *Bull. Ass. belge* (1898), **12**, 279.

²⁴ Goutal. *Compt. rend. Acad. sci.* (1902), **135**, 477; *Ann. chim. anal.* (1903), **8**, 279; *Analyst* (1903), **28**, 128.

²⁵ Noyes, W. A., McTaggart, J. R., and Craver, H. W. *Journ. Am. Chem. Soc.* (1895), **17**, 843; Gill, A. H. *Gas and Fuel Analyses for Engineers*, N. Y. (1902), 90; Hempel, W. *Ztschr. f. angew. Chem.* (1892), **5**, 389.

vary by less than .2 per cent on either side, from those given by the calorimeter.

Other methods have been proposed for the determination of the heating power of coal without the use of the calorimeter. These methods are never more than approximations.

The oldest of these is that of Berthier,²⁶ the determination being made by intimately mixing 1 gram of powdered coal and 50 grams of litharge together in a clay crucible and covering with a layer of salt. The mixture is heated in a crucible furnace, with a gradually increasing heat until fusion is complete; this requires about fifteen minutes. The crucible is removed, poured, and when cold the bottom is cleaned and weighed. Pure carbon should reduce 34 times its own weight of lead; hydrogen 103 times its own weight. One part of pure carbon can raise the temperature of 8,080²⁷ parts of water 1°. If the fuel is assumed as carbon, its value in heat-units may be estimated by multiplying $\frac{8080}{34}$ by the weight of the lead bottom obtained in the assay. As hydrogen is always present in the coal, this method necessarily gives low results.²⁸ Stölzel²⁹ observed that between the results obtained by this method and those calculated from the ultimate analysis there was an almost constant difference; those by Berthier's method being about one-ninth too low. Von John and Fullon³⁰ made a series of comparisons of the results of Berthier's process with those calculated from analysis on European coals. The former were almost uniformly lower than the latter, in some cases 900 calories. In 1895, Noyes, McTaggart, and Craver³¹ compared the results obtained by Berthier's method, on various coals in the calorimeter and by calculation from the ultimate analysis. They corroborate the statements made in previous work that Berthier's method gives low results. "Theoretically, 1 gram of lead should correspond to a heating effect in the coal of 234 calories. The results calculated with this factor are, however, about 12 per cent too low. The average of the results obtained, give an empirical factor of 268.3 calories per gram of lead." The results given were calculated with this empirical formula and agree with those determined by the calorimeter as well as those calculated by Dulong's formula. Munroe³² proposed a "modification of Berthier's process for the valuation of a coal." This has all of the constant error of the conventional process and in general is a more complicated manipula-

²⁶ *Polytech. Journ.*, (Dingler) (1835), 58, 391.

²⁷ Favre, P. A., and Silbermann, J. T. *Ann. chim. et phys.* (1852), III, 34, 403.

²⁸ Langbein, H. *Chem. Ztg.* (1906), 30, 1116, has pointed out that this method will not even give accurate results for coke.

²⁹ Stölzel, C. *Polytech. Journ.*, (Dingler) (1857), 146, 138; *Jahresbr. chem. Technol.* (1858), 3, 499.

³⁰ Von John, C., and Fullon, H. B. *Jahresbr. d. Reichsanst.* (1892), 155; *Ztschr. f. angew. Chem.* (1893), 6, 285.

³¹ Noyes, W. A., McTaggart, J. R., and Craver, H. W. *Journ. Am. Chem. Soc.* (1895), 17, 847; *Analyst* (1896), 21, 22.

³² Munroe, C. E. *Am. Chem. Journ.* (1880-81), 2, 277.

tion. In like manner Lebaigne³³ proposed to grind together 0.2 gram of finely powered coal with 2 grams of pure potassium nitrate. In order to lessen the action of the nitrate on the coal, 5 grams of sodium sulphate are mixed in and the whole slowly melted in a silver crucible. When the mass becomes white, then the heat is gradually increased until it is thoroughly fused. The mass is dissolved in water and titrated with sulphuric acid. In order accurately to determine the heating power of a coal by Berthier's method it would be necessary to determine the relation between the carbon and hydrogen, that is, their percentages by an elementary analysis. It is not surprising that the method has fallen into disuse. However, the process might be of use locally. The coal of a vein or sometimes of an entire region is very similar and a constant empirical factor might be determined which would give good results.

Goutal's formula as originally proposed applies only to coals capable of being analyzed by the official method and was not extended to coals where the percentage of fixed carbon in the pure coal is as low as 50 per cent. Some time ago I attempted to extend the formula of Goutal to Philippine coal.³⁴ It was thought at that time that the coals of this Archipelago were of the same class as many of the bituminous coals of America. However, sufficient data were not then at hand to demonstrate this fact; more recent work has shown them to be of slightly lower grade, the volatile combustible matter to be of slightly lower calorific value and large discrepancies occur in their analyses when made by the official method.³⁵ It is a well-known fact that the quantity and character of the volatile products of a coal are influenced by the conditions of distillation; by the official method of analysis the rise of temperature in the coal is very rapid and more of the coal is volatilized than by the smoking-off method and for this reason if for no other the volatile combustible matter of Philippine coals would appear different from others of the same grade. The calorific value of the fixed carbon of Philippine coal is also slightly lower than that of coking coals. That of pure coke, free from ash, is often greater than that of pure carbon because of the hydrogen from the pitch (hydrocarbon) which characterizes a coking coal, a part of which is always left as the cementing material in the coke. As a rule, the heating value does not differ materially from that of pure anthracite coal. Goutal gives the average for pure anthracite coal as 8250 calories.³⁶ The heating power of a sample of coke is given as follows:

³³ *Répert. d. Pharmac.* (1880) No. 6; *Jahresbr. d. chem. Technol.* (1882), 27, 990.

³⁴ Cox, A. J. *This Journal*, (1906), 1, 877.

³⁵ *Idem*, *Sec. A.* (1907), 2, 41; *Sec. A.* (1908), 3, 301.

³⁶ *Compt. rend. Acad. sci.* (1902), 135, 479. A similar number is given by *The Coal and Metal Miners' Pocket Book*, Scranton, Pa. (1902), 168.

Proximate analysis of the coal.

[The figures give percentages.]

Source of the coal.	Method of analysis.	Water.	Volatile combustible.	Fixed carbon.	Ash.	Sulphur.
Australia -----	Official ³⁷ -----	2.53	36.12	48.99	12.36	0.09
Do -----	do -----	2.53	36.07	48.96	12.44	-----

Analysis of the coke.

[The figures give percentages.]

No.	Source of the coal.	Method of analysis.	Combustible matter. ^a	Ash.	Sulphur.
1	Australia -----	Official -----	79.85	20.15	Trace.
2	do -----	do -----	79.74	20.26	-----

^a By difference.

Calorific value of the coke in calories:

1	2
6550	6562

Calculated calorific value of the pure coke (free from ash):

1	2
8209	8224

The latter results corroborate those of Goutal and substantiate his formula for coking coals, that—

$P = 82C + aV$ where,

P = the heating power in calories.

C = percentage of fixed carbon as determined by analysis.

V = percentage of volatile combustible, as determined by analysis.

a = function of the ratio between the volatile combustible and the total combustible matter in the coal, that is:

$$\frac{\text{per cent of volatile combustible matter}}{100 - (\text{per cent moisture} + \text{per cent ash})}$$

In my previous publication, as was stated, the values for a were given tentatively, as sufficient data were not available thoroughly to test the accuracy of the formula when applied to coals of these Islands. Attention was called to the fact that greater discrepancies between calculated and determined values were noted in the analyses of Philippine coals than in the ones from which the numbers were calculated. A satisfactory explanation was not then at hand, but it is now believed that these were due to the inapplicability of the methods of analysis existing at that time, as will be shown below. The numbers were calculated from American

³⁷ Accurate. Cf. *This Journal*, Sec. A. (1907), 2, 52.

bituminous and subbituminous coals and are applicable only to coals of that class. They are as follows:

When the percentage of volatile combustible as compared with total combustible matter is equal to—	Then a is equal to—
25	102
27.5	97
30	92
32.5	87
35	82
37.5	77
40	72
42.5	67
45	63
47.5	59
50	58
52.5	
55	56

Australian coal is strictly of the class of the American bituminous coal and the use of the formula with the values of a as given above is applicable to it, as is shown by the following table where the determined and calculated results are tabulated side by side:

TABLE I.³⁸

No.	Source.	Water.	Vola- tile com- busti- ble.	Fixed carbon.	Ash.	Total sul- phur.	100 V. C. V.C.+F. C.	Calories.	
								Calor- imeter.	Calcu- lated.
1	Westwaldsend (1905) ..	2.59	32.85	52.97	11.59	-----	38.3	6,687	6,775
2	Westwaldsend (1906) ..	2.60	34.84	52.57	9.99	0.01	39.9	6,976	6,825
3	do	2.44	34.77	45.18	11.61	0.61	43.6	6,128	6,000
4	Westwaldsend (1907) ..	2.80	34.23	50.94	12.03	0.09	40.2	6,614	6,600
5	Westwaldsend (1908) ^a ..	1.74	36.64	52.43	9.19	0.15	41.1	6,983	6,875
6	Westwaldsend (1907) ^b ..	2.56	32.97	51.68	12.79	0.12	38.9	6,472	6,650
7	Westwaldsend (1908) ..	2.80	31.24	54.35	11.61	-----	36.5	6,885	6,920
8	New Westwaldsend (1907).	2.56	35.28	52.46	9.70	0.31	40.2	6,906	6,825
9	Illawarra near Sydney ..	1.26	25.26	63.49	9.99	-----	28.5	7,624	7,600
10	Lichzow Valley (1908) ..	2.11	32.47	52.62	12.80	0.58	38.2	6,987	6,770

^a Selected lump.

^b Double screened and picked twice.

We would anticipate that the Goutal formula using the values of a given above, is applicable to Australian coal, since the latter is of the same class as the 150 American coals from which the values were calculated.

I have devised a chart (fig. 1) which is generally applicable to coals of this class, by means of which the same results may be obtained and the formula and laborious process of calculating entirely dispensed with.

³⁸ Analyses made by the official method (*Journ. Am. Chem. Soc.* (1899), 21, 1116).

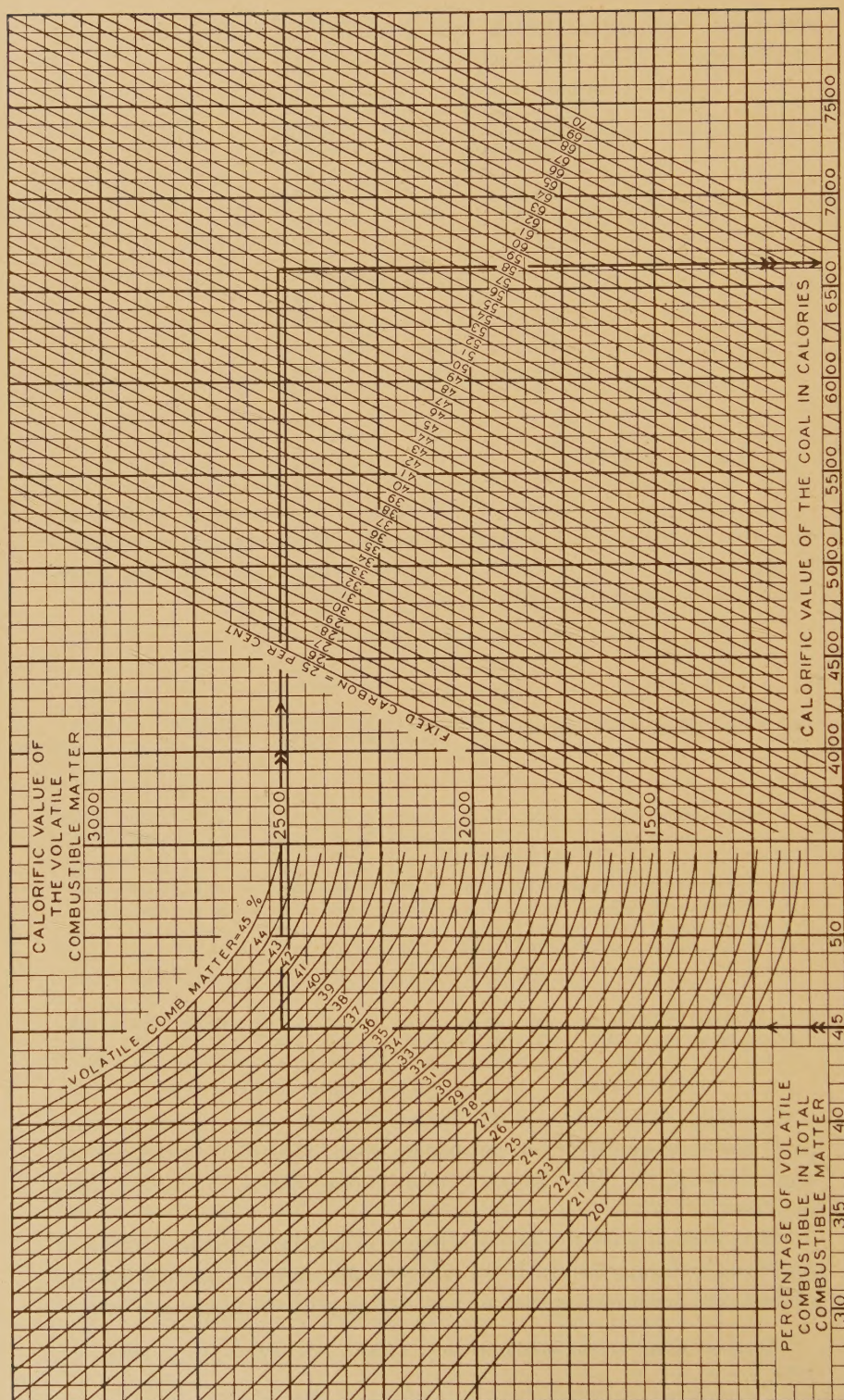


FIG. 1.—Chart for finding the calorific value of bituminous and sub-bituminous coals from their proximate analyses, when analysis by the official method is applicable.

This chart has been drawn on the basis of the Goutal formula with my values for "*a*" given on page 179, and from it the approximate calorific value of the coal may be found, when the proximate analysis as made by the official method is known. The procedure is as follows:

Find from the analysis the percentage of volatile combustible matter in the pure coal ($\frac{100 \text{ V. C. M.}}{\text{V. C. M.} + \text{F. C.}}$). Locate this value on the chart and follow the ordinate (vertical line), until it intersects the curve representing the volatile combustible matter which agrees with the percentage determined in the analysis; continue from this point along the abscissa (horizontal line), until the curve representing the percentage of fixed carbon of the analysis is reached; continue downward on the ordinate to the base line where the calorific value of the coal may be directly read. Example:

Analysis of the coal.

Constituent.	Per cent.
Water	5.75
Volatile combustible matter	40.00
Fixed carbon	50.00
Ash	4.25
Total	100.00

$\frac{100 \text{ V. C. M.}}{\text{V. C. M.} + \text{F. C.}} = 45$, the percentage of volatile combustible matter in the pure coal. Locate 45 on the chart and follow the ordinate as indicated by the arrow until it intersects the curve representing 40 per cent of volatile combustible matter; continue from this point along the abscissa until the curve representing 50 per cent of fixed carbon is reached; continue downward on the ordinate to the base line where the calorific value of the coal may be read as 6,620 calories.

Goutal assumed the calorific value of the fixed carbon of all coal to be 8,200 calories,³⁹ or the share that fixed carbon contributes to the calorific value of coal as eighty-two times the per cent of fixed carbon in the sample. This was substantiated by the determination of the calorific value given above for an Australian coal, but it does not

³⁹ Streit, H. *Dissert. Univ. Zürich* (1906); *Chem. Abs.* (1908), 2, 1040 has shown that the heat of combustion of ash- and moisture-free coke obtained by one and the same method from different coals is the same but differs if different methods are employed. Crucible coke produced by the French (Goutal) method is least degasified, by the American method most; that by the Bochum method occupies an intermediate position. In general the heat of combustion of pure cokes is as follows:

Crucible coke:	Calories.
Goutal	8,230
Bochum	8,160
American	8,100
Gas coke	8,000
Oven coke	7,950

hold good for Philippine noncoking coals as is shown by the following results:

Proximate analyses of the coals.

[The figures give percentages.]

Source of the coal.	Method of analysis.	Water.	Volatile combustible.	Fixed carbon.	Ash.	Sulphur.
Cebú, near Carmen...	Smoking-off ⁴⁰ ...	14.61	35.58	48.16	1.65	0.12
Do.....	do.....	14.71	35.43	48.29	1.57	-----
Polillo.....	do.....	5.88	39.18	48.90	6.04	-----
Do.....	do.....	5.90	39.39	48.75	5.96	-----

*Analyses of the residues from which the volatile matter has been expelled.*⁴¹

[The figures give percentages.]

Source of the coal.	Combustible matter. ^a	Ash.	Sulphur.
Cebu, near Carmen.....	96.69	3.31	Trace.
Do.....	96.85	3.15	-----
Polillo.....	89.01	10.99	-----
Do.....	89.11	10.89	-----

^a By difference.

Calorific value.

[The figures give calories.]

Source of the coal.	Of the residue from which the volatile matter has been expelled.			Of the pure fixed carbon.		
	1.	2.	3.	1.	2.	3.
Cebu, near Carmen...	7,826	7,830	7,815	8,087	8,091	8,076
Polillo.....	7,233	7,239	7,249	8,122	8,128	8,140

The fixed carbon from a powdered sample of most of the known coal of these Islands is somewhat similar to wood sawdust charcoal. It is very granular and it seldom manifests any tendency to sinter together.⁴² The average of the six closely agreeing determinations given above of the calorific value of the pure fixed carbon is 8,107 calories. This is

⁴⁰ Accurate; large mechanical loss by official method.

⁴¹ These samples were obtained by expelling the moisture and volatile combustible matter as outlined in *This Journal*, Sec. A (1907), 2, 44, cooled in a desiccator and weighed directly from the crucible by difference, so that there was no opportunity for the absorption of moisture.

⁴² Recently 2 coking coals have been discovered.

an exceedingly close agreement with the generally accepted number of Berthelot,⁴³ of Petit⁴⁴ or of Favre and Silberman⁴⁵ of 8,140, 8,103, and 8,080 calories, respectively, for pure carbon. The Philippine coals are known to be very low in heavy hydro-carbon compounds⁴⁶ and naturally the fixed carbon would likewise be low, since it would be the more easily degasified. The above results indicate that they are entirely devoid of hydrocarbons that have high heats of combustion, or else that the pure fixed carbon is pure carbon. Therefore, at present it is impossible to establish a generally applicable formula for calculating the heat of combustion of all types of coals from the results of proximate analysis and instead of using eighty-two times the per cent of fixed carbon for its calorific value, for our coals, we must use eighty-one.

Bement says "moisture is the most variable"⁴⁷ factor in Illinois coal and "it is a fact that the coal from a general locality has been analyzed over and over again, with always a more or less different result when presented in only the moist coal composition, so that after all of the multiplicity of work, a final conclusion or full understanding is still unattained."⁴⁸

It is probable that the great variability in the moisture is accountable for the different results. I have shown⁴⁹ that when coal is analyzed according to the official method, a variation of one and a half per cent in the volatile combustible matter, respectively fixed carbon, is produced if the percentage of loosely held water is varied five per cent; moreover, in the analysis of Philippine coal the official method gives large mechanical losses. The smoking off method which was devised and substituted for the official method gives no mechanical loss and also by its use no variation in the fuel ratio is produced when the content of loosely held water is varied. In the light of this research it seems proper to attribute the great discrepancies which were noted in Bement's paper, to error in the method of analysis rather than to inherent properties of the coal.

There are other errors in the proximate analysis of coal which, though recognized, are not often capable of calculation as they represent the sum of a number of variable chemical changes. It was pointed out above that the presence of carbonates in coal introduces the error of high carbon in the ultimate analysis. This is also true of the proximate analysis. Carbonates which give off carbon dioxide, gypsum and silicates which give up their combined water, and pyrites which is converted to iron oxide, when the coal is burned to ash, are all sources of error.

⁴³ Berthelot, *loc. cit.*

⁴⁴ Petit, *loc. cit.*

⁴⁵ Favre, P. A., and Silberman, J. T. *Ann. chim. et phys.* (1852), III, 34, 403.

⁴⁶ Cox, A. J. *This Journal* (1906), 1, 877.

⁴⁷ Bement, A. *Ill. Geol. Surv.* (1906), Bull. 3, 23.

⁴⁸ Bement, A. *Journ. Am. Chem. Soc.* (1906), 28, 637.

⁴⁹ Cox, A. J. *This Journal, Sec. A* (1907), 2, 60.

W. Brinsmaid⁵⁰ has shown that in an Illinois coal each one per cent of ash as weighed equals 1.13 per cent of ash in the coal. 1.13 per cent error on a coal found to contain 10 per cent of ash, is not inconsiderable. As a small offset to this error, the combustion of the sulphur develops some heat, but this is an extremely small factor in Philippine coals.

Great unity in results are obtained with Philippine coals when the smoking-off method of analysis is used.

The proximate analyses and calorific values of most of the known Philippine coals are given in Table II.

⁵⁰ *Journ. Ind. and Chem. Eng.* (1909), 1, 67.

TABLE II.—*Proximate analyses and calorific values of Philippine coals.*

No.	Source. ^a	Water.	Volatile combustible matter.	Fixed carbon.	Ash.	Color of ash.	Total sulphur.	Fuel ratio. ^b V.C.M. + F.C.	Calories.		Variation of the calculated from the determined calories.
									Calorimeter.	Calculated.	
1	Batan Island, eastern end.....	{ 20.81 20.70 }	36.92	35.57	6.70		1.54	0.963	4792	4860	+ 68
2	do.....	{ 20.82 20.40 }	37.10	36.76	5.82		1.59	0.992	4772	4976	+ 204
3	do.....	{ 12.50 12.53 13.89 }	35.68	37.12	14.70	Cream to brown.	0.83	1.033	4578	4912	+ 334
4	Batan Island, north side of eastern end.....	{ 13.89 13.16 20.69 }	35.69	36.94	8.55		1.93	1.003	5221	5266	+ 45
5	Batan Island, south side of eastern end.....	{ 20.69 20.65 19.79 }	36.43	37.88	5.00		0.79	1.039	4790	5021	+ 231
6	do.....	{ 19.79 19.79 15.41 }	36.95	37.81	5.45		1.14	1.023	4862	5049	+ 187
7	Batan Island, Betts (1905).....	{ 15.42 15.42 18.09 }	39.46	41.02	4.11		0.22	1.039	4873	5437	+ 564
8	Batan Island, Betts (April, 1907) ^c	{ 17.97 18.09 18.54 }	36.24	38.44	7.23		0.84	1.050	4647	5165	+ 518
9	Batan Island, Betts (May, 1907) ^c	{ 18.69 21.11 21.15 }	36.72	34.76	9.98			0.955	4560	4736	+ 176
10	Batan Island, Betts (June, 1907) ^c	{ 21.11 21.15 21.15 }	36.72	37.36	4.81			1.017	4820	4994	+ 174

^a These names are arranged alphabetically except those beginning with P, which are placed after those beginning with B for convenience of classification.

^b Fixed carbon.

^c Volatile combustible.

^e Analyzed for me by Mr. H. S. Walker of this laboratory.

TABLE II.—*Proximate analyses and calorific values of Philippine coals*—Continued.

No.	Source. ^a	Water.	Vola- tile com- bust- ible matter.	Fixed carbon.	Ash.	Color of ash.	Total sulphur.	Fuel ratio. ^b	100 V. C. M. V. C. M. F. C.	Calories.		Varia- tion of the cal- culated from the deter- mined calories.
										Calor- imeter.	Calcu- lated.	
11	Batan Island, Military Reservation ^c	{ 6.52 6.42	{ 38.84 39.13	{ 49.12 48.98	{ 5.52 5.47	{ } }	{ } }	{ 1.259 1.435	{ 44.3 41.1	6264	6062	-202
12	do	{ 5.76 5.43	{ 37.15 37.55	{ 58.63 58.57	{ 3.46 3.45	{ } }	{ } }	{ } }	{ } }	6542	6344	-198
13	do	{ 5.76 5.62	{ 41.21 41.34	{ 50.55 50.58	{ 2.48 2.46	{ } }	{ } }	{ 1.225 1.225	{ 44.9 44.9	6385	6307	-378
14	Batan Island, Military Reservation, (coal seam No. 5)	{ 7.42 7.47	{ 37.15 37.36	{ 52.96 52.67	{ 2.47 2.50	{ Yellow to brown }	{ } }	{ 1.271 1.117	{ 44.0 47.2	6255	6274	+ 19
15	Batan Island, Military Reservation	{ 5.18 5.88	{ 40.76 38.28	{ 45.51 49.41	{ 8.55 6.43	{ Buff Brick red	{ } }	{ 0.22 0.09	{ 47.2 43.6	6079	5871	-208
16	do	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	6298	6054	-244
17	do	{ 5.87 5.99	{ 38.99 39.83	{ 50.30 49.86	{ 4.84 4.32	{ do do	{ } }	{ 1.290 1.252	{ 43.7 44.4	6359	6164	-195
18	do	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	6374	6174	-200
19	do	{ 6.07 5.70	{ 39.96 46.30	{ 49.53 40.28	{ 4.44 7.72	{ do Gray	{ } }	{ 1.239 0.870	{ 44.6 53.5	6455	6154	-301
20	do	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	6126	5744	-382
21	Batan Island, Military Reservation (lower seam No. 5)	{ 5.76 5.52	{ 39.64 42.84	{ 51.76 48.68	{ 2.84 2.96	{ Light Yellow	{ } }	{ 1.306 1.136	{ 43.4 52.5	6722	6318	-404
22	Batan Island, Military Reservation (upper seam No. 5)	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	{ } }	6567	6289	-328
23	Batan Island, Military Reservation (seam No. 4)	{ 5.59 5.48	{ 39.69 41.03	{ 53.18 50.81	{ 1.54 2.68	{ } }	{ } }	{ 1.340 1.222	{ 42.7 45.0	6794	6435	-359
24	Borneo, Labuan mines ^d	{ 5.38 5.19	{ 41.03 38.84	{ 50.81 53.12	{ 2.65 2.85	{ } }	{ } }	{ } }	{ } }	6664	6311	-353
25	Polillo	{ 5.04 4.60	{ 39.32 40.03	{ 52.84 52.09	{ 2.80 3.28	{ } }	{ } }	{ 1.355 1.300	{ 42.5 43.5	6573	6386	-187
26	do	{ 4.51 4.87	{ 40.08 39.71	{ 52.01 52.48	{ 3.40 2.94	{ } }	{ } }	{ } }	{ } }	6875	6363	-512
27	do	{ 4.54 4.54	{ 40.06 40.06	{ 52.43 52.43	{ 2.97 2.97	{ } }	{ } }	{ 1.315 1.315	{ 43.1 43.1	6885	6387	-448

28	do	{ 5.88	39.18	48.90	6.04	Red	41.6	6285	6079	-226
29	Polillo, Visita de Burdeuse	{ 5.90	39.39	48.75	5.96					
30	Polillo	{ 5.50	39.30	50.98	4.22	Reddish	43.5	6448	6235	213
31	do	{ 4.36	39.32	52.42	3.90	Red	42.9	6752	6353	399
32	do	{ 4.51	39.49	52.80	3.70					
33	Philippines ^d	{ 5.62	37.83	44.96	11.59	do	45.7	5883	5695	218
34	do	{ 5.62	37.84	44.83	11.71	Brownish red	46.3	6232	5894	338
35	Cebu, near Compostela	{ 6.90	39.95	46.33	5.11	Reddish	48.5	6108	5958	150
36	do	{ 7.13	37.55	48.70	6.85					
37	Cebu, near Cebu (cooking)	{ 6.76	37.24	49.32	6.68	do	48.0	6180	5991	189
38	do	{ 9.48	38.32	51.14	1.06		42.8	6402	6196	206
39	Cebu, Comansi	{ 7.50	37.45	51.31	3.74	do	42.2	6357	6163	194
40	Cebu, Comansi (vein No. 1)	{ 1.42	42.41	48.00	8.17	Brownish red	46.9	7405		
41	Cebu, Comansi (vein No. 2)	{ 1.29	42.02	50.09	6.60		45.6			
42	Cebu, Comansi (vein No. 3)	{ 11.02	38.24	48.05	2.69	Light brown	44.3	6264	5942	322
43	Cebu, near Carmen	{ 7.65	38.36	45.55	8.44		45.7	5943	5746	197
44	do	{ 11.28	38.20	46.76	3.76		45.0	6230	5835	395
45	do	{ 10.71	37.24	46.45	5.60		44.5	6010	5759	251
46	do	{ 14.61	35.58	48.16	1.65	Reddish	42.4	5923	5809	114
47	do	{ 14.71	35.43	48.29	1.57					
48	do	{ 14.38	38.85	39.96	7.31	do	48.7	5248	5289	+ 41
49	do	{ 14.33	37.75	40.28	7.64					
50	do	{ 13.51	35.58	44.49	6.42	Yellow	44.0	5497	5519	22
51	do	{ 13.38	34.90	45.13	6.59					
52	do	{ 15.71	35.48	45.58	3.23	Buff	43.7	5535	5595	60
53	do	{ 15.65	35.30	45.72	3.33					

^a These names are arranged alphabetically except those beginning with P, which are placed after those beginning with B for convenience of classification.

^b Fixed carbon.

^c Volatile combustible.

^d Analyzed for me by Mr. H. S. Walker.

^e Imported by Behn, Meyer & Co. The coal is of the same character and grade as West Batan Island, Polillo, etc., coal.

^f Incipient coking.

^g Exact source unknown but near Polillo.

TABLE II.—Proximate analyses and calorific values of Philippine coals—Continued.

No.	Source. ^a	Water.	Vola- tile com- busti- ble matter.	Fixed carbon.	Ash.	Color of ash.	Total sulphur. ratio. ^b	Fuel ratio. ^b	100 V.C.M. V.C.M.F.C.	Calories.		Vari- ation of the cal- culated from the deter- mined calories.
										Calor- imeter.	Calcu- lated.	
47	Cebu, northern end Danao-Compostela coal field	17.56	32.59	44.41	5.44	—	0.11	1.363	42.3	5293	5344	+ 51
48	do	{ 15.98	{ 33.90	{ 47.04	{ 3.08	{ Buff	{ 0.14	{ 1.388	{ 41.9	{ 5702	{ 5626	— 67
49	do	{ 15.89	{ 33.87	{ —	{ —	{ —	{ —	{ —	{ —	{ —	{ —	{ —
50	do	{ 17.30	{ 32.80	{ 44.10	{ 5.80	{ do	{ 0.09	{ 1.348	{ 42.6	{ 5479	{ 5325	—154
51	do	{ 17.26	{ 32.62	{ —	{ —	{ —	{ —	{ —	{ —	{ —	{ —	{ —
52	do	{ 16.95	{ 34.15	{ 46.71	{ 2.19	{ Red	{ 0.59	{ 1.374	{ 42.1	{ 5661	{ 5615	— 46
53	do	{ 17.03	{ 33.95	{ 46.87	{ 2.15	{ —	{ —	{ —	{ —	{ —	{ —	{ —
54	do	{ 15.86	{ 35.40	{ 47.69	{ 1.05	{ Reddish	{ 0.29	{ 1.348	{ 42.6	{ 5784	{ 5768	— 16
55	do	{ 15.78	{ 35.46	{ 47.85	{ 0.91	{ —	{ —	{ —	{ —	{ —	{ —	{ —
56	do	{ 15.14	{ 34.85	{ 47.93	{ 2.58	{ Buff	{ 0.44	{ 1.392	{ 41.8	{ 5803	{ 5725	— 78
57	do	{ 15.22	{ 34.48	{ 47.90	{ 2.40	{ —	{ —	{ —	{ —	{ —	{ —	{ —
58	do	{ 14.74	{ 34.30	{ 45.35	{ 5.61	{ do	{ 0.53	{ 1.335	{ 42.8	{ 5581	{ 5543	— 38
59	do	{ 14.60	{ 34.25	{ 45.66	{ 5.49	{ —	{ —	{ —	{ —	{ —	{ —	{ —
60	do	{ 15.26	{ 34.59	{ 47.33	{ 2.82	{ Light brown	{ 0.16	{ 1.368	{ 42.2	{ 5719	{ 5688	— 31
61	do	{ 15.32	{ —	{ —	{ 2.78	{ —	{ —	{ —	{ —	{ —	{ —	{ —
62	do	{ 15.08	{ 34.18	{ 49.47	{ 1.27	{ Reddish	{ 0.13	{ 1.444	{ 40.9	{ 5755	{ 5834	+ 79
63	do	{ 15.26	{ 34.25	{ 49.30	{ 1.19	{ —	{ —	{ —	{ —	{ —	{ —	{ —
64	do	{ 14.84	{ 32.93	{ 49.07	{ 3.16	{ Brown	{ 0.88	{ 1.496	{ 40.1	{ 5588	{ 5745	+157
65	do	{ 14.82	{ 32.82	{ 49.28	{ 3.08	{ —	{ —	{ —	{ —	{ —	{ —	{ —
66	do	{ 15.66	{ 34.62	{ 46.85	{ 2.87	{ Buff	{ 0.13	{ 1.351	{ 42.5	{ 5593	{ 5652	+ 59
67	do	{ 15.64	{ 34.73	{ 46.84	{ 2.79	{ —	{ —	{ —	{ —	{ —	{ —	{ —
68	do	{ 18.32	{ 34.93	{ 38.76	{ 7.99	{ Grayish	{ 0.40	{ 1.105	{ 47.5	{ 4860	{ 5011	—151
69	do	{ 18.26	{ 35.10	{ 38.63	{ 8.01	{ —	{ —	{ —	{ —	{ —	{ —	{ —
70	do	{ 18.25	{ 36.93	{ 39.42	{ 5.40	{ Reddish	{ 2.75	{ 1.079	{ 48.1	{ 5108	{ 5188	— 80
71	do	{ 18.06	{ 36.69	{ 39.99	{ 5.26	{ —	{ —	{ —	{ —	{ —	{ —	{ —

60	do	{ 18.06 18.25 }	35.48	40.13	6.33 6.25	{ Light gray Red Light brown Yellow Reddish brown Light yellow Brown Light brown Light gray Brown Gray Buff }	0.96	1.131	46.9	5077	5153	+ 76
61	do	{ 18.03 18.03 18.96 19.06 }	35.44 35.70 36.69 36.59 }	44.28 44.04 40.07	2.25 2.23 4.28		0.43	1.241	44.6	5352	5484	+ 132
62	do	{ 19.06 21.72 21.52 }	36.59 34.58 34.67 }	40.07	4.28		1.43	1.094	47.8	4917	5210	+ 293
63	do	{ 21.72 21.52 }	34.58 34.67 }	40.08	3.02		0.19	1.158	46.3	4863	5103	+ 240
64	do	{ 19.04 19.77 17.33 }	36.01 35.23 38.17 }	40.14 41.59 40.73	4.81 3.41 3.77		1.60	1.115	47.3	4918	5181	263
65	do	{ 19.77 17.33 }	35.23 38.17 }	41.59 40.73	3.41 3.77		0.52	1.181	45.7	4945	5257	312
66	do	{ 20.00 19.95 14.16 14.02 }	35.20 35.19 32.76 32.71 }	41.41 41.25 39.84 39.99 }	3.89 3.61 13.24 11.60		1.34	1.067	48.4	4990	5345	+ 355
67	do	{ 20.00 19.95 14.16 14.02 }	35.20 35.19 32.76 32.71 }	41.41 41.25 39.84 39.99 }	3.89 3.61 13.24 11.60		0.22	1.174	46.0	4817	5235	+ 418
68	do	{ 14.16 14.02 }	32.76 32.71 }	39.84 39.99 }	13.24 11.60		0.46	1.219	45.1	4861	4987	+ 126
69	Cagayan Province, 3 kilometers northeast of Alcala	{ 19.23 1.14 }	38.83 23.46 }	30.29 45.44 }	29.96		0.780	1.937	56.2	4275	4534	+ 239
70	Catanduanes Island (cooking)	{ 25.88 26.86 18.27 18.17 }	32.26 32.44 34.74 34.73 }	32.87 33.05 37.10 37.33 }	7.99 7.65 9.89 9.77				34.0		4938	
71	Dinagat Island	{ 26.86 18.27 18.17 }	32.44 34.74 34.73 }	33.05 37.10 37.33 }	7.65 9.89 9.77		1.019		49.5	4318	4404	86
72	Lepanto-Bontoc, Banaue	{ 11.47 5.75 }	23.87 39.14 }	14.08 50.84 }	50.58 4.27		0.29	1.072	48.3	4564	4878	314
73	Mindanao, near Mati									1749		
74	Mindanao, Zamboanga Peninsula, Sibugney River	{ 16.34 16.35 }	43.87 43.94 }	31.75 31.82 }	8.04 7.89		1.299		43.5	6350	6216	- 334
75	Mindoro	{ 15.34 15.37 17.85 17.84 }	46.02 46.49 42.64 42.64 }	32.50 31.98 37.32 37.32 }	6.14 6.16 2.19 2.20		0.724		58.0	4992	4927	- 65
76	Mindoro, Bulacao (1907) ^a						0.697		58.9	5434	5090	- 344
77	Mindoro, Bulacao, weathered (1907)											
							0.875		53.3	5269	5308	+ 39

^a These names are arranged alphabetically.

^a These names are arranged alphabetically except those beginning with P, which are placed after those beginning with B for convenience of classification.

^b Volatile combustible.

^c Analyzed for me by Mr. H. S. Walker.

^d Specific gravity, 1.34

^e Specific gravity, 1.30.

TABLE II.—*Proximate analyses and calorific values of Philippine coals*—Continued.

No.	Source. ^a	Water.	Volatile combustible matter.	Fixed carbon.	Ash.	Color of ash.	Total sulphur.	Fuel ratio. ^b	100 V. C. M. V. C. M. F. C.	Calories.		Variation of the calculated from the determined calories.
										Calorimeter.	Calculated.	
78	Mindoro, Bulacao (1905)	{ 10.84 10.71	39.70 39.41	47.84 48.27	1.62 1.61	{ Yellowish red	---	1.215	45.2	5569	6012	+ 443
79	Negros, near Cadiz	{ 18.19 18.29	32.03 31.98	31.74 31.77	18.04 17.96	{ White	0.00	0.992	50.2	4008	4288	+280
80	Negros, Escalante	{ 12.97 13.00	37.13 37.29	40.32 40.29	9.58 9.42	{	1.67	0.814	55.1	4903	5258	+355
81	Rizal	{ 9.06 9.01	37.00 39.76	47.99 47.75	5.95 3.48	{	0.46	1.297	43.5	5986	5870	-116
82	Samar, Paranas	{ 9.13 15.24	40.06 45.38	47.81 36.36	3.50 3.02	{ Red	---	1.191	45.6	6124	5989	-135
83	Samar	{ 15.26 15.99	45.29 39.26	36.40 38.21	3.05 6.54	{ Reddish white	---	0.803	55.5	5213	5377	+164
84	Sorsogon, near Montufar	{ 13.62 13.62	42.93 41.35	38.21 39.43	2.10 3.70	{	---	0.973	50.7	4711	5198	+487
85	Sorsogon, near Montufar, picked	{ 12.21 12.38	44.66 44.80	39.43 39.18	3.69	{ Yellow	---	0.963	50.9	5138	5650	+512
86	Tayabas, Atimonan	{ 12.38 6.23	44.80 39.27	39.18 50.72	3.78	{ Red	0.06	0.879	53.2	---	5581	---
87	Zamboanga ^c	---	---	---	---	---	---	1.287	43.7	6199	5770	-429

^a These names are arranged alphabetically except those beginning with P, which are placed after those beginning with B for convenience of classification.

^b Fixed carbon.

^c Volatile combustible.

^d Incipient coking.

In the Goutal formula the second factor of the equation is a function of the ratio between the volatile and the fixed combustible matter. The analytical data given in the preceding table have been recalculated to the ash and water free (pure coal) basis, which shows this ratio, and the results are given in the following table:

TABLE III.

No.	Source.	Fixed carbon.	Volatile combustible matter.
		<i>Per cent.</i>	<i>Per cent.</i>
1	Batan Island, eastern end of -----	49.07	50.93
2	do -----	49.87	50.13
3	do -----	50.92	49.08
4	Batan Island, north side of eastern end -----	50.06	49.94
5	Batan Island, south side of eastern end -----	50.96	49.04
6	do -----	50.57	49.43
7	Batan Island, Betts' (1905) -----	50.96	49.04
8	Batan Island, Betts' (April, 1907) -----	51.22	48.78
9	Batan Island, Betts' (May, 1907) -----	48.85	51.15
10	Batan Island, Betts' (June, 1907) -----	50.43	49.57
11	Batan Island, Military Reservation -----	55.72	44.28
12	do -----	58.93	41.07
13	do -----	55.06	44.94
14	Batan Island, Military Reservation (seam No. 5) -----	58.64	41.36
15	Batan Island, Military Reservation -----	52.75	47.25
16	do -----	56.35	43.65
17	do -----	56.33	43.67
18	do -----	55.59	44.41
19	do -----	55.35	44.65
20	do -----	46.52	53.48
21	Batan Island, Military Reservation (lower seam No. 5) -----	56.63	43.37
22	Batan Island, Military Reservation (upper seam No. 5) -----	47.45	52.55
23	Batan Island, Military Reservation (seam No. 4) -----	57.26	42.74
24	Borneo, Labauan mines -----	55.01	44.99
25	Polillo -----	57.54	42.46
26	do -----	56.51	43.49
27	do -----	56.91	43.09
28	do -----	55.42	44.58
29	Polillo, Visita de Burdeus -----	56.47	43.53
30	Polillo -----	57.06	42.94
31	do -----	54.27	45.73
32	do -----	53.70	46.30
33	Philippines -----	56.46	43.54
34	do -----	56.98	43.02
35	Cebu, near Compostela -----	57.16	42.84
36	do -----	57.82	42.18
37	Cebu, near Cebu -----	53.09	46.91
38	do -----	54.38	45.62
39	Cebu, Camansi -----	55.68	44.32
40	Cebu, Camansi (vein No. 1) -----	54.28	45.72
41	Cebu, Camansi (vein No. 2) -----	55.04	44.96
42	Cebu, Camansi (vein No. 3) -----	55.50	44.50
43	Cebu, near Carmen -----	57.60	42.40
44	do -----	51.32	48.68

TABLE III—Continued.

No.	Source.	Fixed carbon.	Volatile combustible matter.
		<i>Per cent.</i>	<i>Per cent.</i>
45	Cebu, near Carmen.....	55.98	44.02
46	do.....	56.33	43.67
47	Cebu, northern end Danao-Compostela coal field.....	57.68	42.32
48	do.....	58.12	41.88
49	do.....	57.42	42.58
50	do.....	57.88	42.12
51	do.....	57.42	42.58
52	do.....	58.20	41.80
53	do.....	57.17	42.83
54	do.....	57.78	42.22
55	do.....	59.07	40.93
56	do.....	59.93	40.07
57	do.....	57.47	42.53
58	do.....	52.50	47.50
59	do.....	51.90	48.10
60	do.....	53.08	46.92
61	do.....	55.39	44.61
62	do.....	52.23	47.77
63	do.....	53.65	46.35
64	do.....	52.71	47.29
65	do.....	54.14	45.86
66	do.....	51.62	48.38
67	do.....	54.00	46.00
68	do.....	54.95	45.05
69	Cagayan Province, northeast of Alcala.....	43.82	56.18
70	Catanduanes Island.....		(*)
71	Dinagat Island.....	50.47	49.53
72	Lepanto-Bontoc, Banaueg.....	51.72	48.28
73	Mindanao, near Mati.....		(*)
74	Mindanao, Zamboanga peninsula.....	56.50	43.50
75	Mindoro.....	41.99	58.01
76	Mindoro, Bulalacao (1907).....	41.07	58.93
77	Mindoro (1907), weathered.....	46.67	53.33
78	Mindoro (1908).....	54.85	45.15
79	Negros, near Cadiz.....	49.80	50.20
80	Negros, Escalante.....	51.99	48.01
81	Rizal.....	56.47	43.53
82	Samar, Paranas.....	54.36	45.64
83	Samar.....	44.52	55.48
84	Sorsogon, near Montúfar.....	49.32	50.68
85	Sorsogon, near Montúfar (selected).....	49.06	50.94
86	Tayabas, Atimonan.....	46.77	53.23
87	Zamboanga.....	56.28	43.72

* On account of very high ash, are probably not normal samples.

These results, which express the ratio of the volatile combustible matter to the fixed carbon are represented graphically by fig. 2.

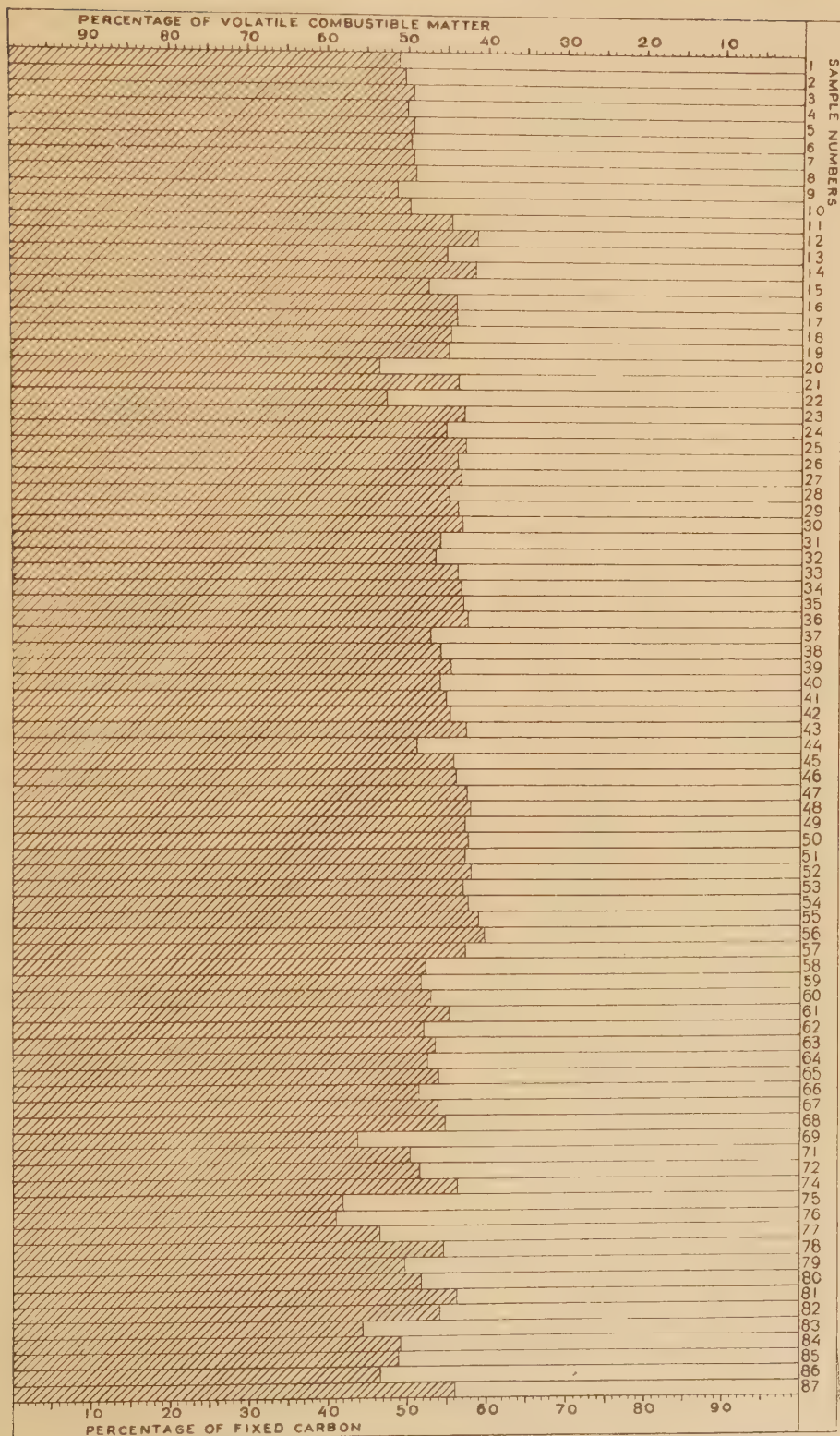


FIG. 2.—Chart showing the ratio of the volatile combustible matter to the fixed carbon in Philippine coals when calculated free from water and ash (pure coal).

The relative amounts of fixed carbon and volatile combustible matter vary very little as is shown by the figure. The coals given are representative of all the Islands and we can assume the average as a fair representation of Philippine coals. Not only the amount, but also the calorific power of the gaseous portion of these coals is approximately the same in all varieties. The following results (Table IV) regarding the calorific value of the volatile combustible matter of coals from this Archipelago have been calculated from work already published.

TABLE IV.

Source of coal.	Yield of gas per kilo of total combustible matter—		Per cent of vola- tile com- busti- ble matter in the total com- busti- ble matter.	Yield of gas per kilo of vola- tile com- busti- ble matter.	Calorific value of the gas produced per kilo of vola- tile com- bustible matter in calories.
	In liters.	Calorific value in calories.			
Batan Island -----	335	$1.4 \cdot 10^6$	50.45	665	$2.8 \cdot 10^6$
Cebu -----	307	$1.5 \cdot 10^6$	51.45	597	$3.0 \cdot 10^6$
Negros -----	297	$1.6 \cdot 10^6$	51.1	581	$3.1 \cdot 10^6$
Zamboanga -----	309	$1.8 \cdot 10^6$	45.4	680	$3.8 \cdot 10^6$
Polillo -----	333	$1.9 \cdot 10^6$	46.6	714	$4.0 \cdot 10^6$

The numbers representing the calorific value of the gas produced per kilo of combustible matter and also of volatile combustible matter in calories are nearly, though not absolutely, constant.⁵¹ The coals from the Military Reservation in Batan Island, from Polillo, and from the Compostela region in Cebu have a somewhat higher value, while that for all others thus far investigated is practically constant. The samples are arranged in the order of the slightly increasing value of the calorific power, and it will be seen from Table IV that the numbers representing the percentage of volatile combustible matter arrange themselves almost in the reverse order.

I have calculated the values of "a" in Philippine coals from the proximate analyses and determined calorific values given in Table II and using as the calorific power of the fixed carbon the value $81 \times$ the percentage, the results are as follows:

⁵¹ The gas from Australian coal has a somewhat higher calorific value than any of the above.

TABLE V.

	Batan Island Military Reserva- tion, 13 samples.	Polillo, 8 samples.	Compos- tela, 6 samples.	All others, 58 samples.
	58.8	58.4	59.0	-----
	58.9	66.4	58.8	-----
	62.8	64.8	62.0	-----
	53.1	59.4	57.7	-----
	58.7	59.0	63.9	-----
	60.0	63.7	63.0	-----
Value of "a" -----	58.6	59.4	-----	-----
	58.6	62.0	-----	-----
	61.1	-----	-----	-----
	61.8	-----	-----	-----
	63.8	-----	-----	-----
	61.3	-----	-----	-----
	62.6	-----	-----	-----
Average -----	60.0	61.6	60.7	50.0

The above averages confirm the facts brought out by actual comparison of the calorific value of the gas. The volatile combustible matter in the coal from the Military Reservation on Batan Island, from Polillo, and from the Compostela region in Cebu has a somewhat higher calorific value than from the others.

For the following percentages of volatile combustible matter in the pure coal the results are as follows:

TABLE VI.

40-42 per cent.		42-43 per cent.		43-44 per cent.		44-45 per cent.		45-46 per cent.		46-48 per cent.		48-50 per cent.		50-52 per cent.		52-58 per cent.	
No.	"a"	No.	"a"	No.	"a"	No.	"a"	No.	"a"	No.	"a"	No.	"a"	No.	"a"	No.	"a"
12	58.9	23	62.6	16	60.0	11	58.8	31	59.4	15	58.7	3	44.2	1	51.8	20	61.8
14	53.1	25	58.4	17	58.6	13	62.8	40	58.7	32	62.0	4	51.1	2	48.1	22	61.2
48	55.8	30	63.7	21	63.8	18	58.6	65	44.7	58	49.3	5	47.3	9	47.6	69	46.9
52	55.9	35	59.0	26	66.4	19	61.1	68	49.7	60	51.5	6	48.5	79	44.8	75	55.1
55	51.3	36	58.8	27	64.8	24	62.1	78	42.4	62	45.6	7	39.3	80	44.0	76	61.0
56	48.8	43	56.8	29	59.0	28	59.4	82	57.0	63	46.7	8	42.2	84	41.2	77	52.7
-----	-----	47	52.0	33	57.6	39	62.0	-----	-----	64	46.3	10	48.9	85	41.7	83	50.0
-----	-----	49	58.3	34	58.7	41	63.9	-----	-----	67	41.7	44	52.5	-----	-----	86	32.2
-----	-----	50	54.9	46	51.9	42	63.0	-----	-----	-----	-----	59	51.1	-----	-----	-----	-----
-----	-----	51	54.0	74	62.1	45	53.0	-----	-----	-----	-----	66	44.3	-----	-----	-----	-----
-----	-----	53	54.7	81	56.7	61	49.9	-----	-----	-----	-----	71	50.9	-----	-----	-----	-----
-----	-----	54	57.4	87	53.5	-----	-----	-----	-----	-----	-----	72	44.6	-----	-----	-----	-----
-----	-----	57	51.9	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
-----	-----	a54.0	-----	a57.1	-----	a59.4	-----	a59.5	-----	a56.0	-----	a50.2	-----	a47.1	-----	a45.6	-----
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

^a Average.

The above figures perhaps show that there is an increase in the calorific value of the volatile combustible matter with a decrease in the percentage, but the difference in any event is very slight and there are many weak points in such a deduction. I believe the assumption that it is constant for all known Philippine coals to be equally accurate. When a technical problem is concerned and it is the desire to draw a general conclusion, it is always necessary to attempt to determine a middle value which will serve all samples equally well. If sufficient data were at hand we probably would derive a slightly smaller value for "a" for the larger percentages of volatile combustible matter in the above table. This would give the highest degree of accuracy.⁵² However, after considering the remarkable regularity and similarity of the Philippine coal,⁵³ the data regarding which have been brought out in this paper, and which also have been continually observed in the researches of this laboratory, and using the data given by Table VI, an average value for "a" has been derived for our coals, namely 53.6; that is, the variable factor "a" becomes a constant for coals of this Archipelago and is expressed by the value 53.6. It is somewhat less than that applicable to coking coals of the same grade.

We now have all the factors for the development of an equation for the calculation of the fuel value of a Philippine coal from its proximate analysis. This formula is as follows:

$$P=81C+53.6V, \text{ where}$$

P=The calorific value in calories,

C=The percentage of fixed carbon,

V=The percentage of volatile combustible matter.

The coals must be analyzed by the "smoking-off method"⁵⁴ which is the only one giving reliable results with Philippine coals. In most cases there is fairly close agreement between results calculated by the use of the formula and those actually determined in the calorimeter; this is shown by Table II, where they are given side by side. It is possible to point out the limits of error by using the foregoing results obtained directly by the calorimeter and calculated by the use of the formula. The average discrepancy between the determined and the calculated heat of combustion of the coals is about 200 calories or nearly four per cent, while the maximum deviation in the case of three or four

⁵² Results already published (Cox, A. J. *This Journal* (1906), 1, 892 et seq.) show that the volatile matter of Philippine outcrop coals contains variable proportions of noncombustible matter other than water which probably accounts for the observed irregularities.

⁵³ The results sometimes suggest the possibility of these beds all having been continuous at one time, the differences in them as we now find them having been produced by metamorphism and other conditions since the breaking up.

⁵⁴ *This Journal*, Sec. A. (1907), 2, 41.

highly weathered outcrop samples is about 500 calories. When it is definitely known that a sample is from one of the regions enumerated in Table V, then it would be more accurate to use the average value for "a" there given, and the discrepancies between the calorimeter and the calculated calories would be greatly reduced.⁵⁵ Such a degree of accuracy gives a good working formula and is as close an agreement as is to be found between many of the calorimeters in actual use to-day. Should future development and deeper boring prove that better coal exists in these Islands and that this formula is no longer applicable, let it be remembered that the data from which this formula is derived are not changed one iota. In a recent publication Constam and Rougeot⁵⁶ conclude that a variation for the same coal of over three per cent may be expected. They used a Parr calorimeter, which is in wide use in America for this work. Lunge and Grossmann⁵⁷ discuss the paper of Constam and Rougeot and state that an apparatus which varies 100 calories is sufficiently accurate for technical purposes. The results of my formula do not greatly exceed these limits and are fairly satisfactory when we consider that two independent samples of the same coal show as great variation as this.

The heating value of the upper bed Philippine coals may be easily determined by the chart given in fig. 3, when the results of the proximate analyses are known. The intersection of that ordinate, which corresponds to the proper percentage of fixed carbon (respectively volatile combustible matter) in the total combustible matter read on the abscissa, with the curve representing the percentage of water and ash in the coal, designates the abscissa which in turn indicates the calorific value given on the ordinate.

Authors⁵⁸ sometimes recommend corrections or modifications of the present analytical methods used in the determination of the composition of coal, such as that the chemical tests be limited to the determination of the ash and the heating power of the pure coal, abandoning in the future the determination of the moisture, volatile matter, fixed carbon, sulphur and evaporating power of the coal.⁵⁹ These, when sifted down

⁵⁵ The physical and chemical properties, the character, the water content (Kohr, O. *Chem. Ztg.* (1908), **32**, 580, Cöthen) and the color of the ash (Knappe, G. *ibid.*, 657) may be of assistance in verifying the locality from which a coal comes. Such observations are especially valuable on samples purporting to be from well established coal fields.

⁵⁶ Constam, E. J. and Rougeot, R. *Ztschr. f. angew. Chem.* 1906, **19**, 1805.

⁵⁷ Lunge, G. and Grossmann, H. *Ibid.*, 1963.

⁵⁸ Bement, A. *Eng. Record* (1906), Oct. 27, 473.

⁵⁹ Our present methods for the proximate analysis of coal probably had their origin in the "immediatanalyse" of L. Gruner (*Ann. Mines* (1873), III, **2**, 511; **4**, 169; *Polytech. Journ.*, (Dingler) (1874), **213**, 73.) who believed that the simplest and safest method of ascertaining the real value of a coal was the determination of the water, coke, and ash.

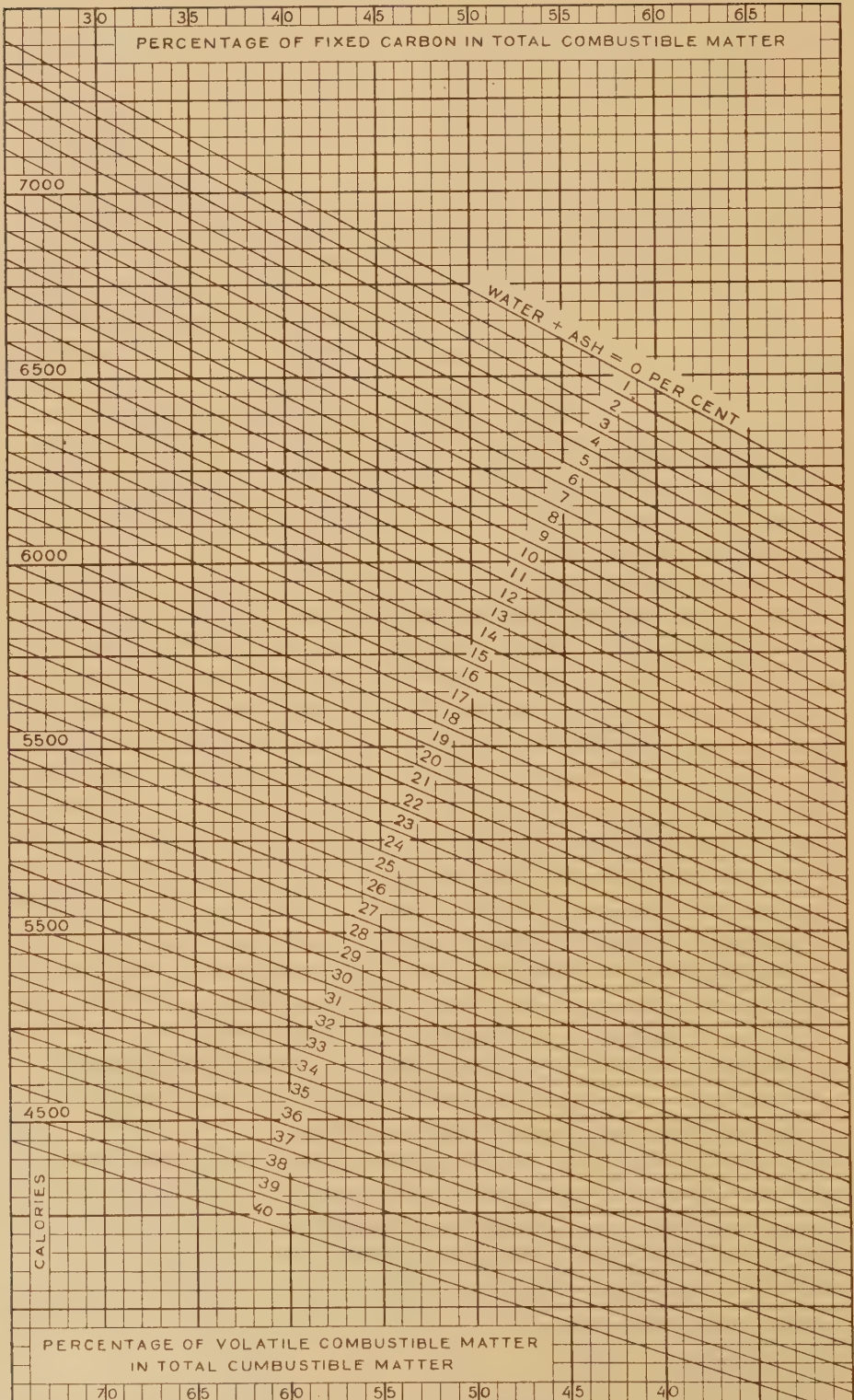


FIG. 3.—Chart for finding the calorific value of Philippine coals when the proximate analyses are known.

often have originated from a misconception of the moisture in coal. Moisture as ordinarily determined is indeed variable, but is of great importance. The coal-testing plant of the United States Geological Survey⁶⁰ have advanced in the right direction in reporting their results in two ways, first, upon the sample as received and secondly, upon the air-dried coal. Almost every coal seam has an amount of water which is characteristic of the coal itself and this has an important significance in the estimation of the value of the fuel; this is indicated by the amount of moisture in the air-dried coal. The difference between this value and the sample as received at the laboratory gives the amount of water which is variable with the exposure of the coal, the season of the year, the state of the weather, the temperature, etc., or perhaps the wetting it has received at the hands of an unscrupulous dealer. In 1866, Reder⁶¹ carried on some interesting experiments with regard to the variation in weight of coal and coke produced by rain, when they are transported in open railway cars. He found that they increased in weight under the conditions of his experiments from 4.6 to 9.6 per cent after from one to five days' exposure. If the plan of the coal-testing plant⁶² is followed consistently, the confusion with regard to the moisture in coal will disappear and the interpretation of the results be simplified. However, usually the purchaser wishes to know how much water is in the ton of coal which he buys, regardless of how it came there. It is the same inert body with respect to the fuel value of the coal in any event, and the heating power of the sample is lowered approximately in proportion to the quantity of this present, as well as by the percentage of ash. The calculation of the results to the basis of dry coal is very simple, if that is a more satisfactory basis for specification.

Even from a practical standpoint it is of great importance to know the amount of volatile and fixed combustible matter in coals. This plan for the analysis of coal was originally formulated when the bulk of the coal used was coking and it was desirable to know the amount of coke that could be produced from a given coal. However, this is a natural distinction and is very useful for noncoking coals, for the two kinds of combustible matter differ in heating power. The calorific value of the fixed carbon is nearly the same for all coals, but that of the volatile combustible matter is very variable for widely different coals. If the specifications in the purchase of coal should be made on a basis of the dry coal, it is still necessary to determine the moisture in order to calculate the amount of coal received. If it is more intelligible to

⁶⁰ Somermeier, E. E. *Journ. Am. Chem. Soc.* (1906), 28, 1630.

⁶¹ Reder, *Ztschr. d. Vereins deutscher Eisenbahnverwaltungen* (1866), No. 43; *Polytech. Centralbl.* (1866), N. F. II, 20, 1447; *Jahresb. d. chem. tech.* (1867), 12, 723.

⁶² Somermeier, *loc. cit.*

the mechanical engineer to have results reported on such a basis, the interpretation from an ordinary proximate analysis and the recalculation of the calorific value of the coal as analyzed are easily made. To the geologist and chemist the present commercial method is more satisfactory than the suggested modifications and it also gives all that is required to determine the value of coal as a commercial commodity.

REFERENCES TO THE LITERATURE OF CALORIMETERS.

- ANDREWS, T. *Phil. Mag. & Journ. Sci.* (1848), III, 32, 321; *Ann. d. Phys. u. Chem.*, (Poggendorff) (1848), 75, 27, 244.
- ATWATER, W. O., and WOODS, C. D. *Report Storrs (Conn.) Exper. Sta.* (1894), 135; Atwater, W. O. and Blakesley, O. S. *Ibid.* (1897), 199; Atwater, W. O. and Snell, J. F. *Journ. Am. Chem. Soc.* (1903), 25, 659; cf. Fries, J. A. *Ibid.* (1909), 31, 272.
- BARRUS, G. H. *Trans. Am. Soc. Mec. Eng.* (1893), 14, 816 (Lewis Thompson's calorimeter improved).
- BERTHELOT, M. *Compt. rend. Acad. sci.* (1880), 91, 188; (1892), 115, 201; *Ann. chim. et phys.* (1878), V, 13, 5; (1881), 23, 160; (1885), VI, 6, 546; (1887), 10, 433; (1888), 13, 289; cf. *Ibid.* (1873), IV, 29, 94 to 186; (1875), V, 5, 5; cf. Stohmann, F. Kleber, Cl. and Langbein, H. *Ztschr. f. angew. Chem.* (1896), 9, 486; *Journ. f. prakt. Chem.* (1889), N. F. 39, 597.
- BOLLEY, P. *Schweizerische polytech. Ztschr.* (1865), 10, 18; *Ztschr. f. anal. Chem.* (1865), 4, 234; *Handbuch der technisch-chemischen Untersuchungen* (1876), 528.
- BOUGHTON, L. F. *Power* (1906), 26, 524.
- BUNSEN, R. *Ann. d. Phys. u. Chem.*, (Poggendorff) (1870), 141, 1; cf. Andrews, *Ibid.* (1871), 142, 320; Bunsen, *Ibid.*, 616; Bohn, C. *Ibid.*, 618; Schuller, A. and Wartha, V. *Ber. d. deutschen chem. Ges.* (1875), 8, 1011.
- CARPENTER, R. C. *Trans. Am. Soc. Mec. Eng.* (1895), 16, 320; cf. Zahn, G. H. B. *Ztschr. f. Ing.* (1897), 1446; *Ztschr. f. angew. Chem.* (1898), 11, 116.
- DESPRETZ, C. *Ann. chim. et phys.* (1824), II, 26, 337; (1828), 37, 180; *Ann. d. Phys. u. Chem.*, (Poggendorff) (1828), 12, 519.
- DULONG, M. *Compt. rend. Acad. sci.* (1838), 7, 871; *Ann. d. Phys. u. Chem.*, (Poggendorff) (1838), 45, 461; *Chem. Centralbl.* (1839), 10, 92.
- EMERSON, C. J. *Journ. Ind. & Eng. Chem.* (1909), 1, 17.
- FAVRE, P. A., and SILBERMANN, J. T. *Ann. chim. et phys.* (1852), III, 34, 403; 36, 1; cf. Thomsen, J. *Ber. d. deutschen chem. Ges.* (1869), 2, 701; (1871), 4, 591; (1872), 5, 614; Favre, *Ann. chim. et phys.* (1872), IV, 26, 385; 27, 265; (1873), 29, 87; Berthelot, M. *Ibid.* (1872), 26, 529; 27, 533.
- FISHER, F. *Polytech. Journ.*, (Dingler) (1879), 232, 341; 233, 135; 234 390; (1885), 258, 330; *Ber. d. deutschen chem. Ges.* (1879), 12, 1694; *Ztschr. f. angew. Chem.* (1899), 12, 334.
- FRANKLAND, E. (Devised by Lewis Thompson but modified by Frankland) *Phil. Mag. & Journ. Sci.* (1866), IV, 32, 182; *Jahresbr. f. Chem.* (1866), 732; cf. Thompson, L.
- GOTTLIEB, E. *Journ. f. prakt. Chem.* (1883), 28, 399.
- GRASSI, C. *Journ. de Pharm.* (1843), 8, 170; *Ann. d. Chem.*, (Liebig) (1845), 56, 185.
- HEMPEL, W. *Ztschr. f. angew. Chem.* (1892), 5, 389; (1896), 9, 486; *Journ. Soc. Chem. Ind.* (1893), 12, 179.

- LANGBEIN, H. *Ztschr. f. angew. Chem.* (1900), **13**, 1235 *et seq.*; cf. Berthelot, *loc. cit.*
- MAHLER, P. *Compt. rend. Acad. sci.* (1891), **113**, 774; *Bull. Soc. encourag. ind. nat.* (1892), **91**, 317 to 374; *Contribution à l'étude des Combustibles*, Paris, Librairie polytechnique Baudry et Comp. (1893); *Journ. Soc. Chem. Ind.* (1892), **11**, 840; *Ztschr. f. angew. Chem.* (1892), **5**, 491; cf. Stohmann and others, *Journ. f. prakt. Chem.* (1894), N. F. **49**, 100.
- PARR, S. W. *Journ. Am. Chem. Soc.* (1900), **22**, 646.
- SCHEURER-KESTNER, A. Method described, *Bull. industr. Mulhouse* (1868), 712.
- SCHWACKHOFFER, F. *Ztschr. f. anal. Chem.* (1884), **23**, 453.
- STOHMANN, F. (Frankland's improved) *Journ. f. prakt. Chem.* (1879), N. F. **19**, 115; (1885), **31**, 273; *Landwirthschaftl. Jahrbücher* (1884), **13**, 513; cf. v. Rechenberg, C. *Journ. f. prakt. Chem.* (1880), N. F. **22**, 244.
- THOMPSON, L., *Chem. news* (1881), **43**, 135; *Journ. Soc. Chem. Ind.* (1886), **5**, 581; *ibid.* (1888), **7**, 868; *Bull. Soc. industr. Mulhouse* (1888), 506; cf. Frankland, also Barrus, *loc. cit.*
- THOMPSON, W. *Journ. Soc. Chem. Ind.* (1886), **5**, 581; (1889), **8**, 525.
- THOMSEN, J. Thermochemische Untersuchungen, **2**; *Ann. d. Phys. u. Chem.*, (Poggendorff) (1873), **148**, 180, 368 (not suited for solid substances).
- URE, A. *Ann. d. Phys. u. Chem.*, (Poggendorff) (1840), **75**, 48.
- VÖLCKNER, C. *Ztschr. d. österr. Ingenieur- u. Architektenvereins* (1882), 31; *Jahresbr. d. chem. Technol.* (1883), **28**, 483.
- WILLIAMS, H. J. *Pop. Sci. Monthly* (1899), Aug.

To the above may be added the very early imperfect forms which are of interest only from an historical point of view.

- CRAWFORD, Experiments and observations on animal heat, London (1788); Dalton, *Ein neues System des chemischen Theils der Naturwissenschaft*, Berlin (1812), 87; Davy, *Essay on Heat, Light, etc.* (1799); Works II, London (1836); Lavoisier and Laplace (ice calorimeter), *Histoire de l'Académie de France* (1781), 379; *Oeuvres de Lavoisier*, II; Rumford, *Ann. d. Phys.*, (Gilbert) (1813), **45**, 1; (1814), **46**, 225; *Phil. Trans. Roy. Soc. London* (1798), **88**, 80.
- FISHER, F. *Polytech. Journ.*, (Dingler) (1879), **234**, 390; *Chem. Centralbl.* (1880), III, **11**, 97 has critically collected the methods and apparatus for the determination of the heating power of fuels, giving a description of some of the early calorimeters brought into use after the ones given above; and v. Knorre, G. *Chem. Ind.* (1894), **17**, 93 and 125 has collected some of the latter literature.

ILLUSTRATIONS.

- FIG. 1. (In text.) Chart for finding the calorific value of bituminous and sub-bituminous coals from their proximate analyses, when analysis by the official method is applicable.
2. (In text.) Chart showing the ratio of the volatile combustible matter to the fixed carbon in Philippine coals when calculated free from water and ash (pure coal).
3. (In text.) Chart for finding the calorific value of Philippine coals when the proximate analyses are known.

THE ECONOMIC POSSIBILITIES OF THE MANGROVE SWAMPS OF THE PHILIPPINES.

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In the United States, and in other countries where large amounts of leather are manufactured, the forests yielding native tanning materials have been so far exhausted that these nations must look to other countries for their source of supply. At the present time very large quantities of tan barks and cutch are imported into the United States from Borneo, Dutch East Africa, Brazil and other tropical countries, and the use of mangrove tanning materials is constantly increasing. The most abundant source of tanning substances in the Philippines is the mangrove swamps of the Islands. At the present time there is no mangrove bark exported from the Philippines, and as yet the area of these swamps is not known. They occur as narrow fringes along the coast or in considerable areas at the mouths of large rivers, especially at the head of bays. Some limited areas have been mapped and measured by the Forestry Bureau. These are as follows:

(1) Island of Mindoro, about 10,000 hectares, which will yield approximately 50,000 tons of bark.

(2) The east coast of the Zamboanga Peninsula, Mindanao, contains about 9,000 hectares of mangrove swamp; this will yield at least 90,000 tons of bark, found on a coast line about 45 miles in length. In the same region, on the other side of the Gulf of Subuguay, there are probably 9,000 hectares more which will also yield at least 10 tons per hectare. With the exception of a number of areas of 1,000 hectares or less, no further regions have been examined carefully. The above statement gives a very small proportion of the total area of the mangrove swamps. It is believed that the swamps of Mindanao alone will yield enough bark to furnish a continuous supply to a very large cutch factory.

The tan barks of Mindanao average from 23 to 25 per cent of tannin, and these are the best that have thus far been examined from the Islands. Such bark could not be profitably shipped to the United States to compete with the East African barks carrying 50 per cent of tannin. A careful analysis of conditions shows that the only method of handling the tan barks commercially is by means of a cutch factory at the source of supply and it appears that such a factory could be operated very profitably, as soon as there is free trade between the Philippines and

the United States. At the present time the United States imposes a duty of seven-eighths of a cent per pound on cutch. The Bureau of Forestry could grant to a company running a cutch factory a twenty-year license agreement to exploit large areas of timber, provided that they carry on the work economically. These grants might be made on the following general conditions:

(1) All trees destroyed must be used for firewood or for timber. The firewood industry of the Islands is a very important one, and could be carried on in connection with the gathering of the bark. During the past fiscal year, taxes were paid on 192,526 cubic meters of firewood. Any company could probably make contracts with small cutters of firewood to obtain the bark at a very low price. The mangrove swamps of Mindanao also furnish valuable timber which is marketed at the present time usually in the shape of telegraph poles. These are known to yield as high as 29,000 board feet of lumber per hectare. One company now lumbering in these swamps does not use the bark at all, and would be glad to dispose of it at a low price.

(2) Restrictions as to cutting should be imposed to insure reproduction. This would be a help rather than a hardship, because it would insure a perpetual supply of bark to the company. The figures of yield of bark given above are based on the cutting of trees 25 centimeters and over in diameter, and are very conservative. In many places clean cutting would be permitted, and then the yield would be much greater. All restrictions made would depend on the condition of the swamp at the time the cutting begins. At the present time, the mangrove barks are assessed on an arbitrary value of 3 pesos (1.50 dollars United States currency) per 100 kilos, and this value may be changed on three months' notice. The bark is known to sell in the provinces for as low as 1 peso per 100 kilos. During the past fiscal year taxes were collected upon 1,847 tons of tan barks of which probably 90 per cent consisted of mangrove barks. These mangrove barks are used in tanning carabao hides, and to a minor extent, for coloring rice.

All the species of mangrove trees of the eastern tropics, which are used commercially for tanning purposes, are also found in the Philippines. These are:

- Rhizophora mucronata* Lam.
- R. conjugata* L.
- Bruguiera gymnorhiza* Lam.
- B. eriopetala* W. & A.
- B. parviflora* W. & A.
- B. caryophylloides* Blume.
- Ceriops tagal* (Perr.) C. B. Robinson.

There are three large cutch factories in Borneo using tan barks from the same species of mangrove as those found in the Philippines. These factories regard the process of manufacturing cutch as a trade secret, but we can not believe that these so-called trade secrets are of a very formidable nature, as we have succeeded in preparing very good grades

of cutch without any complicated processes in this laboratory. Our cutch is a dry, brown solid with a brilliant, almost metallic, fracture. It is easily and completely soluble in water and the analysis shows the following constituents:

Constituent.	In parts per 100 of water-free material.	
	I.	II.
	Per cent.	Per cent.
Moisture.....	2.6	5.7
Insoluble.....	1.9	1.3
Soluble.....	98.1	98.7
Non Tannin.....	28.8	26.1
Tannin.....	69.3	72.6

The following was the method used to prepare the cutch:

The finely ground bark was leached with cold water, and this solution evaporated to dryness *in vacuo*. Hot water extracts too much of the coloring matter, and no more tannin than cold water. The evaporation, at least the latter stages, must always be made *in vacuo* to avoid burning the cutch. It is sufficiently obvious that the extraction on a large scale would be carried out in such a manner that strong solutions would be employed to leach fresh bark while weak ones would be used to extract the last percentages of the tannin from the partly exhausted bark. All the parts of the factory, except the vacuum dryers, could be built on the ground, and it is evident that the fuel for the boilers and for the dryers would cost very little, so that it would appear that if the cutch manufacture were taken up in connection with the lumbering or firewood industry that it would be exceedingly profitable.

Tables of analyses made on mangrove tan barks are given below. It will be noted that the barks from Mindanao run very much higher in tannin than those from Mindoro, and it has often been observed that, as the equator is approached, the tannin percentage increases. The analyses below were made by the methods of the International Leather Chemists Association, using the American "shake modification." As our machine does not give very violent shaking and as we have used unchromed hide powder, it is possible that our results may be as much as 2 per cent low. We are now taking measures to standardize our analyses with those made by a recognized leather chemist and in a subsequent communication will report several hundred analyses of mangrove tan barks from the southern islands, so that perfectly reliable data will be at hand for possible investors in this field.

Botanical determinations of the mangrove bark samples: First lot, from Mindoro. Mr. Merrill of the Botanical Section of this Bureau made the identifications. The botanical material was very poor and was not preserved.

Second lot, from Zamboanga, collected by Dr. H. N. Whitford and W. I. Hutchinson of the Bureau of Forestry in January, 1908.

Forestry Bureau No.	Field No.	Common name.	Scientific name.
9356	2056	Tabique -----	<i>Xylocarpus obovatus</i> A. Juss.
9357	2057	Tangal -----	<i>Ceriops tagal</i> (Perr.) C. B. Robinson.
9358	2058	Bacauan -----	<i>Rhizophora mucronata</i> Lam.
9359	2059	Pototan -----	<i>Bruguiera parviflora</i> W. & A.
9360	2060	Pototan -----	<i>Bruguiera gymnorrhiza</i> Lam.

Third lot, from Mindoro, collected by M. L. Merritt, of the Bureau of Forestry in March, 1908.

Forestry Bureau No.	Field No.	Common name.	Scientific name.
9779	1911	Bacauan -----	<i>Rhizophora conjugata</i> L.
9780	1912	Bacauan -----	Do.
9781	1913	Hagalay -----	<i>Bruguiera parviflora</i> W. & A.
9782	1914	Pototan -----	<i>Bruguiera gymnorrhiza</i> Lam.
9783	1915	Bacauan -----	<i>Rhizophora mucronata</i> Lam.
9795	1921	Tangal -----	<i>Ceriops tagal</i> (Perr.) C. B. Robinson.
9816	1922	Tangal -----	Do.
9851	1984	Tangal -----	Do.

TABLE I.—Analysis of barks from Port Banga, Zamboanga.

Forestry Bureau No.	Field No.	Common name.	Scientific name.	Moisture (per cent).	In parts per 100 of water-free bark.			
					Insolubility (per cent).	Total extract (per cent).	Non-tannin (per cent).	Tannin (per cent).
9356	2056	Tabique ----	<i>Xylocarpus obovatus</i> A. Juss -----	14.9	69.7	30.3	8.6	21.7
9357	2057	Tangal ----	<i>Ceriops tagal</i> (Perr.) C. B. Robinson. -----	12.4	65.2	34.8	11.6	23.2
9358	2058	Bacauan ----	<i>Rhizophora mucronata</i> Lam -----	14.4	61.7	38.3	12.4	25.9
9359	2059	Pototan ----	<i>Bruguiera parviflora</i> W. & A -----	13.9	84.1	15.9	7.1	8.8
9360	2060	Pototan ----	<i>Bruguiera gymnorrhiza</i> Lam -----	16.1	63.0	36.96	9.8	27.2
		Tabique ----	<i>Xylocarpus obovatus</i> A. Juss -----	14.2	67.6	32.4	7.7	24.7

These barks were collected on January 1908 by Dr. H. R. Whitford and W. I. Hutchinson from Port Banga, Zamboanga. They are rather large quills with thick, harsh, dirty brown scales on the outer surface. Tabique gave a very dark, red infusion; tangal a somewhat light red infusion; bacauan gave an intense red infusion. Pototan (*Bruguiera parviflora*) is a fibrous bark difficult to grind; it gave a red infusion. Pototan (*Bruguiera gymnorrhiza*) gave the same colored infusion as the previous one.

TABLE II.—Analysis of barks from Mindoro.

Forest- ry Bu- reau No.	Field No.	Common name.	Scientific name.	Mois- ture (per cent).	In parts per 100 of water-free bark.			
					Insol- ubility (per cent).	Total ex- tract (per cent).	Non- tan- nin (per cent).	Tan- nin (per cent).
9779	1911	Bacauan	<i>Rhizophora conjugata</i> L.	13.2	67.4	32.6	12.0	20.6
9780	1912	do	do	14.4	66.6	33.4	10.7	22.7
9781	1913	Hangalay	<i>Bruguiera parviflora</i> W. & A.	14.0	77.4	22.4	9.6	12.8
9782	1914	Pototan	<i>Bruguiera gymnorrhiza</i> Lam.	13.9	60.2	39.8	11.6	28.2
*9783	1915	Bacauan	<i>Rhizophora mucronata</i> Lam.	13.2	64.3	35.7	14.1	21.6
9795	1921	Tangal	<i>Ceriops tagal</i> (Perr.) C. B. Robinson	11.8	69.1	30.9	9.7	21.2
9816	1922	do	do	12.3	72.5	27.5	10.5	17.0
9851	1984	do	do	12.7	71.5	28.5	8.0	20.5
*9780	1912	Bacauan	<i>Rhizophora conjugata</i> L.	13.5	64.8	35.2	10.8	24.4
	1912½	do	do	14.1	67.1	32.9	10.0	22.9
	*1913½	Hangalay	<i>Bruguiera parviflora</i> W. & A.	14.8	75.5	24.5	9.6	14.9
	1913½	do	do	12.9	82.1	17.9	8.3	9.6
	1914½	Pototan	<i>Bruguiera gymnorrhiza</i> Lam.	13.9	63.4	36.6	12.6	24.0
	*1915½	Bacauan	<i>Rhizophora mucronata</i> Lam.	13.4	67.1	32.9	15.1	17.8

* Analysis of inner bark.

The barks were collected by Mr. M. L. Merritt in Mindoro in March 1908. Bacauan bark is brittle and is very easily ground. It has a dirty brown scale of variable thickness which is very easily removed from the true or inner bark.

Analyses were made on both entire and inner bark of each variety. In every case inner bark showed a higher percentage of tannin than when entire bark was assayed.

Bacauan numbered 1912 contained approximately 10 per cent outer scale.

Bacauan infusions were red, but varied in intensity.

The Hangalay barks are reddish-brown in color with rough, dark brown scales.

The inner bark of Hangalay is fibrous and the ground bark was very irritating to the mucous membranes of the nose and throat when inhaled. They also gave red infusions.

Barks of Pototan and Tangal also possess rough, brownish scales.

The infusions were somewhat lighter than those of Bacauan.

TABLE III.—Analysis of barks from Port Banga, Zamboanga.

Field No.	Common name.	Scientific name.	Mois- ture (per cent).	In parts per 100 of water- free bark.			
				Insol- ubility (per cent).	Total ex- tract (per cent).	Non- tan- nin (per cent).	Tannin (per cent).
11534	Bacauan	<i>Rhizophora conjugata</i> Lam.	13.4	68.7	31.3	13.3	18.0
11535	Tangal	<i>Ceriops tagal</i> (Perr.) C. B. Robinson	11.9	58.6	41.4	19.1	22.3
11536	Pototan	<i>Bruguiera gymnorrhiza</i> Lam.	13.5	62.0	38.0	13.5	24.5
11537	Lañgaray	<i>Bruguiera parviflora</i> W. & A.	13.8	80.4	19.6	8.0	11.6

This table shows results of analysis made on another lot of barks from Port Banga, Zamboanga, collected by H. N. Whitford on December, 1908.

TABLE IV.—*Analysis of mangrove barks from Sarawak, Borneo.*

Common name.	Scientific name.	Moisture. (per cent.).	Insolubility (per cent.).	Total extract (per cent.).	Non-tannin (per cent.).	Tannin (per cent.).
Gayong.....	<i>Rhizophora mucronata</i> Lam.....	14.4	70.1	29.9	9.4	20.5
Bakô	<i>Rhizophora conjugata</i> Lam.....	14.7	58.3	41.7	9.6	32.0
Putut.....	<i>Bruguiera gymnorhiza</i> Lam.....	15.5	64.3	35.7	9.0	26.7
Tumu	<i>Bruguiera eriopetala</i> W. & A.....	16.1	64.0	36.0	8.8	27.2
Tangal	<i>Ceriops tagal</i> (Perr.) C. B. Robinson	13.8	63.8	36.2	6.9	29.3

Analysis was made of some samples of mangrove barks brought from Sarawak, Borneo by Dr. Foxworthy of the botanical division of this Bureau. These barks are used by cutch factories and among the species in Borneo probably yield the highest amount of tannin.

PHILIPPINE RAW CEMENT MATERIALS.¹

By ALVIN J. COX.

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The essential constituents of Portland cement are calcium oxide (CaO), silica (SiO_2), and alumina (Al_2O_3) or some other flux such as ferric oxide which, similarly to alumina is able to promote the union of silica and lime. Calcium oxide does not occur in nature in the free state, but in combination as calcium carbonate (limestone, chalk, etc.). Silica and alumina are found in the form of minerals such as quartz and corundum, but in this form they are not suitable for the manufacture of cement, owing to the difficulty of grinding the materials to a sufficiently fine state to cause them to combine with lime; therefore, combinations of these two oxides occurring as silicates of alumina, termed clay or shale, are the chief source of these constituents in the raw materials used in cement manufacture. The majority of limestones contain some clay, and clays often contain a certain amount of limestone, these facts are taken into account in proportioning the raw materials.

RAW CEMENT MATERIALS ON THE ISLAND OF BATAN.

Limestone occurs abundantly on nearly every Island of the Philippine Archipelago and in this region is uniformly remarkably pure. On the other hand, suitable shale or clay for the manufacture of a high grade Portland cement is more difficult to obtain. It will be seen by referring to any of the military records of drill holes made when prospecting for coal on Batan Island with a standard diamond 2-inch core drill, that the holes penetrate thick layers of grayish-blue shale separated by more or less thin layers of fossil or calcareous shale and limestone. It was thought that analyses of these blue shales might show the variation to be expected, reveal the presence of some materials not otherwise easily accessible and that they would help to form an opinion as to what, if any, siliceous cement materials exist on this island. The beds encountered are not horizontal; the dip indicates that they outcrop somewhere on the island. If these are suitable for the purpose of cement

¹The first discussion of this subject was published in *This Journal*, Sec. A. (1908), 3, 391.

manufacture, the material might be easily available. On the other hand, if the proper constituents were to be found, these shales might be mined after the manner adopted by some successful cement companies now operating.

The samples were obtained from a drill hole made in the Moncao basin on the left bank of the river about 1.5 kilometers from its mouth and at an elevation of 5.8 meters.

A vertical section of the drill hole shows:

Material.	Thickness.	Total depth of hole.
	<i>Meters.</i>	<i>Meters.</i>
Surface clay.....	1.8	1.8
Blue shale.....	22.5	24.3
Limestone.....	0.3	24.6
Fossil shale.....	5.6	30.2
Blue shale.....	17.9	48.1
Limestone.....	9.1	57.2
Blue shale.....	4.6	61.8
Shale and limestone.....	6.0	67.8
Blue shale.....	7.7	75.5
Shale and limestone.....	3.1	78.6
Blue shale.....	1.0	79.6
Shale and limestone.....	3.5	83.1
Limestone.....	2.9	86.0
Shale and limestone.....	7.7	93.7
Limestone.....	4.4	98.1
Shale and limestone.....	3.4	101.5
Limestone.....	8.6	110.1
Blue shale.....	1.5	111.6
Limestone.....	2.3	113.9
Blue shale.....	19.1	133.0
Limestone.....	0.6	133.6
Blue shale.....	0.3	133.9
Limestone.....	0.8	134.7
Blue shale.....	6.5	141.2
Shale and limestone.....	1.2	142.4
Limestone.....	1.5	143.9
Blue shale.....	39.9	183.8
Limestone.....	0.3	184.1
Shale and limestone.....	2.4	186.5
Limestone.....	4.5	191.0
Shale and limestone.....	1.6	192.6

The chemical analyses of some of the materials are given in Table I. I also give the average of the analyses of two limestones which agree very closely in composition; these were taken from drill holes numbers 5 and 6.

TABLE I.—*Analyses of shales and limestones from Batan Island.*

	1.	2.	3.	Lime- stone.
Depth in meters.....	1.8-48.1	57.2-61.8	114-133	
Silica (SiO ₂).....	42.72	35.02	34.80	0.97
Alumina (Al ₂ O ₃) ^a	17.23 ^b	13.21	11.70	0.56
Ferric oxide (Fe ₂ O ₃).....	2.13	2.13	2.69	0.25
Ferrous oxide (FeO).....	4.11	3.49	3.47	0.11
Lime (CaO).....	11.12	17.44	17.19	53.86
Magnesia (MgO).....	3.65	2.84	2.84	0.19
Soda (Na ₂ O).....	0.87	1.29	1.46	
Potash (K ₂ O).....	1.44	0.68	0.80	0.16
Loss on ignition ^c	^d 15.58	^d 17.50	17.19	43.18
Water below 110°.....	1.85	5.31	4.90	0.30
Titanium oxide (TiO ₂).....	^b Above.	0.77	0.95	
Sulphuric anhydride (SO ₃).....	None.	None.	None.	
Sulphur (S).....	0.44	0.61	0.61	
Manganese (MnO).....		Trace.	0.09	
Correction.....			^e 1.45	
Total.....	101.14	100.29	100.14	
Less O=S.....	0.22	0.31	0.31	
Total.....	100.92	99.98	99.83	99.58

^a Includes possible phosphoric anhydride (P₂O₅).

^b Includes titanic oxide (TiO₂).

^c A number of chemical changes are involved in this factor including both losses and gains, and the amount of these depends largely on the temperature employed. With the crucible covered and a moderate heat, carbon dioxide, water and carbonaceous matter are entirely driven off, the sulphides are oxidized to sulphates and all the sulphur is retained as sulphates by the calcium. With continued heating at a slightly higher temperature all of the iron is oxidized. With intense heat the sulphates are gradually decomposed with the ultimate loss of the entire sulphur and the alkalies are volatilized.

^d Ignited so that very little if any oxidation occurred.

^e For the oxidation of the sulphur and ferrous iron on ignition.

About two years ago, W. A. Aiken proposed a theoretical analysis for Lehigh district cement as follows:

	Per cent.
Minimum silica (SiO ₂)	21
Maximum alumina (Al ₂ O ₃)	9
Maximum iron (Fe ₂ O ₃)	3.25
Lime (CaO)	62.5-63.25
Maximum magnesia (MgO)	3.0

In order to confirm this theoretical analysis, Mr. Aiken² made very thorough tests on fourteen brands of Portland cement in the laboratory of the New York Subway Construction. Eight of these brands showed an average analysis practically in agreement with the theoretical one; the remaining six failed to comply with the minimum silica and three of these failed to comply with the theoretical

² Concrete, 8, No. 2, 33 to 34.

analysis by excess of lime. The best results are shown by the eight brands that agree closely with the theoretical analysis.

Mr. Aiken has continued his work and taken samples from several Portland cement mills. He³ gives results of the tests of these different brands and says "The results herein given certainly emphasize the fact that much cement is of the best and that *there is no monopoly of material* or proportioning in manufacture, as shown by these tests of average output from eight different brands, three of them *not Lehigh district material*."

Portland cement was thought by Le Chatelier⁴ to be composed of tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$, and tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. In 1897 S. B. and W. B. Newberry⁵ showed that this idea should be modified to dicalcium aluminate $2\text{CaO} \cdot \text{Al}_2\text{O}_3$ since the latter showed superior qualities. Richardson⁶ and other investigators have concurred in the opinion that tricalcium silicate is an essential constituent of Portland cement; recently, however Day and Sheperd⁷ have shown rather conclusively that no such compound as tricalcium silicate exists and therefore the so-called tricalcium silicate is simply a mixture of lime and dicalcium silicate. The only rational deductions from these facts are those given by R. K. Meade,⁸ namely: "That the lime in Portland cement clinker exists in three forms: *First*, in combination with silica, alumina, iron, etc., to form a magma of orthosilicates, $2\text{CaO} \cdot \text{SiO}_2$, orthoaluminates, $2\text{CaO} \cdot \text{Al}_2\text{O}_3$, etc.; *second*, as the oxide itself in solid solution in this magma of silicates, aluminates, etc., and *third*, as undissolved oxide; that is lime merely disseminated through the magma forming with the latter simply a mechanical mixture." The fact remains that under the most ideal conditions of fluxing and burning, a cement will carry an amount of lime very nearly corresponding to the Le Chatelier molecular formula as modified by Newberry and Newberry, viz., $x [(3\text{CaO})\text{SiO}_2] + y [(2\text{CaO})\text{Al}_2\text{O}_3]$. Overlimed cements are unsound, but up to this point the more lime that is present the greater will be the strength of the cement. Bleining, as mentioned in my previous paper⁹ has shown from his experiments that "for the dry, ground mixtures the formula $(2.8 \text{ CaO})\text{SiO}_2(2\text{CaO})\text{Al}_2\text{O}_3$ is the safest." Even this give a percentage of lime in the burned product higher than that encountered in many cements.

Magnesium not to exceed three or four per cent of the finished product may replace calcium in Portland cement without deleterious results, and iron in any amount may replace alumina.¹⁰ A certain amount of iron acts as a flux, lowers the fusion point of the mixture and promotes the combination of the calcium oxide and silica. Several articles have recently appeared in the literature advocating the superiority of a cement for use in sea water, in which practically all of the alumina

³ *Concrete Review* 2, No. 11, 2 to 7.

⁴ *Ann. des Mines* (1887), 11, 345.

⁵ *Journ. Soc. Chem. Ind.* (1897), 16, 887.

⁶ Address, Assoc. Portland Cement Manufacturers, Atlantic City, N. Y., June 15th, 1904; *Journ. Soc. Chem. Ind.* (1905), 24, 733.

⁷ *Journ. Am. Chem. Soc.* (1906), 28, 1107.

⁸ *Chem. Eng.* (1907), 5, 344.

⁹ *This Journal, Sec. A.* (1908), 3, 405.

¹⁰ Newberry, S. B. and W. B.: *Journ. Soc. Chem. Ind.* (1897), 16, 891.

is replaced by iron and showing that iron-ore cement has been used with efficiency for such works of construction.¹¹

If the international atomic weights for 1909 are used in the above limiting molecular formula of Bleiningger, then for every part by weight of silica 2.60 of calcium oxide are required, for every part of alumina 1.10 of calcium oxide, for every part of ferric oxide 0.70 of calcium oxide, and for every part of ferrous oxide 0.78 of calcium oxide. As the clay itself contains a certain proportion by weight of calcium oxide, this amount must be deducted from the total required (the amount of magnesian present is equivalent to 1.4 its weight of calcium oxide). On the other hand, the limestone contains silica, alumina and oxides of iron which take up some of the calcium and accordingly reduce the amount available.

The calculation of a cement mixture from shale number 1 and the limestone would be as follows:

SHALE.

$42.72 \times 2.60 = 111.07$ parts calcium oxide required by silica in 100 parts shale.

$17.23 \times 1.10 = 18.95$ parts calcium oxide required by alumina in 100 parts shale.

$2.13 \times 0.70 = 1.59$ parts calcium oxide required by ferric oxide in 100 parts shale.

$4.11 \times 0.78 = 3.21$ parts calcium oxide required by ferrous oxide in 100 parts shale.

134.82 parts calcium oxide required by 100 parts shale.

$11.12 + (3.65 \times 1.4) = 16.23$ parts calcium oxide equivalent to calcium and magnesium in 100 parts shale.

(1) 118.59 parts calcium oxide to be added to 100 parts shale.

LIMESTONE.

$53.86 + (0.21 \times 1.4) = 54.13$ parts calcium oxide equivalent to calcium and magnesium in 100 parts limestone.

$0.97 \times 2.60 = 2.52$	} 3.40 parts calcium oxide in 100 parts limestone which is not available.
$0.56 \times 1.10 = 0.62$	
$0.25 \times 0.70 = 0.17$	
$0.11 \times 0.78 = 0.09$	

(2) 50.73 parts calcium oxide available in 100 parts limestone.

$\frac{(1)}{(2)} = \frac{118.59}{50.73} = 2.34$ parts limestone required by 1 part shale.

The limestone and shale number 1 combined according to this calculation give the following results:

¹¹ Newberry, S. B.: *Cement Age*, 4, 38; *Monthly Consular and Trade Report* (1908), June, 165; *Cement and Eng. News* (1908), 20, 112, 168.

TABLE II.

[The numbers give parts of the material by weight.]

	Total.	Individual constituents.					
		Silica (SiO ₂).	Alu- mina (Al ₂ O ₃).	Iron oxide ^a (Fe ₂ O ₃).	Cal- cium oxide (CaO).	Mag- nesium oxide (MgO).	Volatile (CO ₂ , H ₂ O, etc.).
Limestone-----	234	2.27	1.31	0.87	126.03	0.44	101.74
Shale No. 1-----	100	42.72	17.23	6.69	11.12	3.65	17.43
Unburned-----	334	44.99	18.54	7.56	137.15	4.09	119.17
Volatile-----	119.2						
Burned-----	214.8	20.95	8.63	3.52	63.85	1.90	-----

^a Estimating all of the iron as ferric oxide.

The limestone and shale number 2 calculated after the same method give the following results:

TABLE III.

	Total.	Individual constituents.					
		Silica (SiO ₂).	Alu- mina (Al ₂ O ₃).	Iron oxide ^a (Fe ₂ O ₃).	Cal- cium oxide (CaO).	Mag- nesium oxide (MgO).	Volatile (CO ₂ , H ₂ O, etc.).
Limestone-----	174	1.69	0.97	0.64	93.72	0.33	75.65
Shale No. 2-----	100	35.02	13.21	6.00	17.44	2.84	22.81
Unburned-----	274	36.71	14.18	6.64	111.16	3.17	98.46
Volatile-----	98.5						
Burned-----	176.5	20.8	8.03	3.76	62.98	1.80	-----

^a Estimating all of the iron as ferric oxide.

The limestone and shale number 3 combined according to a similar calculation give the following results:

TABLE IV.

	Total.	Individual constituents.					
		Silica (SiO ₂).	Alu- mina (Al ₂ O ₃).	Iron oxide ^a (Fe ₂ O ₃).	Cal- cium oxide (CaO).	Mag- nesium oxide (MgO).	Volatile (CO ₂ , H ₂ O, etc.).
Limestone-----	171	1.66	0.96	0.63	92.10	0.32	74.35
Shale No. 3-----	100	34.80	11.70	6.54	17.19	2.84	22.09
Unburned-----	271	36.46	12.66	7.17	109.29	3.16	96.44
Volatile-----	96.4						
Burned-----	174.6	20.9	7.25	4.11	62.60	1.81	-----

^a Estimating all of the iron as ferric oxide.

The limiting formula given above does not give entire satisfaction, since there are two undetermined variables. Limits for the silica-alumina (respectively iron oxide) ratio must also be set.

E. D. Campbell¹² has shown in his experiments that the best cements were produced from lean clays high in silica, with a ratio $3 > 1$. He says "the substitution of Al_2O_3 , or Fe_2O_3 for SiO_2 , that is, the use of a rich clay, lowers the overburning temperature" that with lean clays heavily limed there is a wide margin between the proper clinkering temperature and the overburning temperature, while with rich clays great care must be exercised in order to prevent overburning.

Bleining¹³ says, "The clay must have a percentage ratio of silica to alumina of from 3 to 1 to 4 to 1" and in drawing conclusions from his own work, continues¹⁴ "The ratios of silica to alumina given on several occasions seems to be correct, for the safest cements in the boiling test, though not the highest in the tensile test are those with a silica-alumina ratio of from 3 to 1 to 4 to 1. *Aluminous cements* are to be condemned." Experiments of this Bureau¹⁵ lead to the conclusion that the composition of Portland cement best adapted for use in a tropical climate should have a high silica-alumina ratio; that is, at least 3 parts of silica to 1 part of alumina. R. K. Meade¹⁶ places the limits for a freshly made American Portland cement as follows:

	Per cent.
Silica	20-24
Alumina	5- 9
Iron oxide	2- 4
Lime	60-63.5
Sulphur trioxide	1- 2

Le Chatelier¹⁷ places the limits of the amount of individual constituents usually present in good commercial Portland cement as follows:

	Per cent.
Silica	21-24
Alumina	6- 8
Iron oxide	2- 4
Lime	60-65
Magnesia	0.5- 2

The above calculations show that cements agreeing nicely with the theoretical analysis for Lehigh district cement could be produced from materials such as those taken from the drill hole on Batan Island. On the other hand, the silica-alumina ratio is low and the composition of the burned product shows that this would barely come within the highest limits proposed by Meade and Le Chatelier. I am of the opinion that it would be found necessary to add silica to the materials in some shape to produce a wholly satisfactory cement.

¹² *Journ. Am. Chem. Soc.* (1902) **24**, 969.

¹³ The manufacture of Hydraulic Cements, *Bull. Geol. Sur.*, Ohio 4th Ser. (1904), **3**, 223.

¹⁴ *Ibid.*, 237.

¹⁵ Reibling, and Salinger, L. A. *This Journal, Sec. A.* (1908), **3**, 185.

¹⁶ *Chem. Eng.* (1907), **5**, 349.

¹⁷ *Trans. Am. Inst. Min. Eng.* (1893), **32**, 16.

Attention might also be called to the fact that owing to a relatively large amount of calcium oxide contained in these shales themselves, only a comparatively small amount of limestone would have to be combined with them and therefore a much larger deposit than is usual for ordinary siliceous shales, would be necessary for a given output.

THE RAW MATERIALS OF MOUNT LICOS REGION, NEAR DANAOS, CEBU.

Although a few borings have been made, there is little doubt but that there is a large supply of raw materials in the Mount Licos region the quality can be ascertained from the following pages. The map of the Danao-Compostela coal district¹⁸ shows the extent of the limestone. Mount Licos is capped with a white, orbitoidal limestone, 30 to 150 meters thick. Limestone occurs abundantly in more or less detached areas over the whole region as remnants of what was most probably originally a continuous blanket. The shales and sandstone are mapped under one color (blue). Dr. Smith has estimated that the total thickness of the coarse, gray sandstone and the coal measure shales, including five coal seams, is 90 to 150 meters¹⁹; this also includes the shales which have locally been weathered to clay. The lower part of the coal measures consists of gray shales and the upper portion of the coarse, gray sandstone. The dip of the beds is naturally with the coal, which varies upward from 20°. Some of the outcrops of the siliceous materials are obliterated by covers of talus, others may be followed all the way up the mountain side, whereas still others have been uncovered or more exposed by railway cuts and mine drifts. The samples here discussed represent large quantities, but were chosen rather to indicate what is known of the character of the materials of the region than to represent any particular bed. A knowledge of its chemical composition is of first importance in the investigation of the suitability of a material for the manufacture of a hydraulic cement and the data for the clays, shales and limestone given in Table V will give the information required.

DESCRIPTION OF SAMPLES.

No. 1. Clay from a short distance beyond the upper terminus of the railway of the Insular Coal Company.

No. 2. Clay found under the Danao coal.

No. 3. Shale dried at 105° C.

No. 4. Calcareous shale from railway cut about 300 meters east of the terminus.

No. 5. Shaly limestone.

No. 6. Shaly limestone from the cut of the railway about 500 meters east of the terminus.

No. 7. Upper limestone from Mount Licos. Especial attention is called to the absence of magnesium.

¹⁸ Smith, W. D. *This Journal*, Sec. A. (1907), 2, 405.

¹⁹ *Ibid*, 390.

TABLE V.—*Analyses.*

[The numbers give percentages.]

Constituent.	1.	2.	3.	4.	5.	6.	7.
Silica (SiO_2)	60.17	43.38	53.35	44.35	29.00	24.02	0.38
Alumina (Al_2O_3) ^a	22.65	29.44	24.11	20.26	11.38	7.49	0.18
Iron oxide (Fe_2O_3) ^b	4.66	0.48	9.03	4.64	5.35	2.00	
Calcium oxide (CaO)	0.31	9.50	0.80	11.37	26.25	33.88	55.62
Magnesia (MgO)	1.85	0.61	2.22	2.59	0.65	2.12	0.00
Alkalies ($\text{K}_2\text{O} + \text{Na}_2\text{O}$)		1.56			1.98		
Loss on ignition	6.35	10.75	8.72	14.30	23.00	28.25	43.50
Water (H_2O) below 110° C	(c)	5.30	(c)	(c)	3.84	(c)	0.17

^a Includes possible titanium oxide (TiO_2).^b Total iron determined as ferric oxide.^c Included under loss on ignition.

These materials may be combined, according to the method of calculation outlined under the preceding head. If clay number 1 is combined with limestone number 7, the formula would require 3.28 parts of limestone to every part of clay and the results would be as follows:

TABLE VI.

[The numbers give parts of the materials by weight.]

	Individual constituents.						
	Total.	Silica (SiO_2).	Alu- mina (Al_2O_3).	Iron oxide (Fe_2O_3).	Cal- cium oxide (CaO).	Mag- nesia (MgO).	Volatile (CO_2 , H_2O , etc.).
Clay (No. 1)	100	60.17	22.65	4.66	0.30	1.85	6.35
Limestone (No. 7)	333.5	1.27	0.60		185.49		143.25
Unburned	433.5	61.44	23.25	4.66	185.80	1.85	151.99
Volatile	152.0						
Burned	281.5	21.83	8.26	1.65	66.00	0.66	

It will be noticed from the parts by weight (percentage composition) of the burned product that the content of lime is higher than that of the average Portland cement. The results of the formula represent the maximum of lime which a cement can carry, if it were manufactured under ideal conditions. In actual practice these are seldom met with and it is therefore necessary to carry the lime lower than that indicated by the formula. Furthermore, a cement which has a comparatively low overburning temperature is always burned at the lowest possible point and at this temperature will usually not carry the maximum quan-

tity of lime. A mixture which would more nearly correspond to the theoretical analysis of Lehigh Portland cement given above is as follows:

TABLE VII.

[The numbers give parts of the materials by weight.]

	Total.	Individual constituents.					
		Silica (SiO ₂).	Alu- mina (Al ₂ O ₃).	Iron oxide (Fe ₂ O ₃).	Cal- cium oxide (CaO).	Mag- nesia (MgO).	Volatile (CO ₂ , H ₂ O, etc.).
Clay (No. 1)-----	100	60.17	22.65	4.66	0.3	1.85	6.35
Limestone (No. 7)-----	292	1.05	0.5	-----	162.6	-----	127.65
Unburned-----	392	61.22	23.15	4.66	162.9	1.85	134.
Volatile-----	134						
Burned-----	258	23.7	8.97	1.80	63.1	0.72	-----

While the limiting formula is of great assistance in the proportioning of cements, it leaves undetermined the silica-alumina ratio, which is of utmost importance. There is every reason to believe that clay number 1 would produce a better cement if silica in some shape were added to the clay base. With the substitution of a certain amount of silica for alumina or iron oxide, molecule for molecule, in the limiting formula a safer cement would be produced in that the overburning temperature would be increased.²⁰ The state of subdivision of the free silica in the raw materials used for this purpose is an extremely important consideration. The sandstones of the region, although high in silica, are probably not suited for this purpose in that they are composed of oxides of iron and alumina and quartz grains so large as to be unsuited to cement manufacture.

This sandstone, which contains approximately 73 per cent silica, when pulverized to the degree necessary for rock analysis and one gram digested in 200 cubic centimeters of 5 per cent sodium hydroxide for 45 minutes on a water bath, allowed 7.6 per cent of the silica to pass into solution.²¹ It is unnecessary to resort to physical means to determine that the greater part of the silica is crystalline, for the quartz grains are visible to the naked eye and very distinct with a lens. The grains are very loosely held together and can be broken apart by rubbing be-

²⁰ The ideal mixture can not be overburned.

²¹ Quartz is not absolutely insoluble in caustic alkalies (Lunge, G. and Millberg, C.: *Ztschr. f. angew. Chem.* (1897), **10**, 393, 425), as is sometimes supposed to be the case and the use of a dilute solution of the latter does not give a correct separation of quartz and amorphous silica, however the error can generally be neglected. Hillebrand (*Bull. U. S. Geol. Sur.* (1907), **305**, 166), recommends as the most satisfactory the use of a dilute solution of sodium hydrate in which the solution of the amorphous silica is almost immediate.

tween the fingers, or gently in a mortar. The state of subdivision will be seen from the following numbers:

Sieve.		Per cent.	
Size.	Meshes per centimeter.	Passed.	Not passed.
100	40	45	55
80	32	57	43
60	24	76	24
50	20	94	6
40	16	98½	1½

A large formation of schist occurs on the Island of Romblon; this is so high in silica that it is doubtful if it could be used alone for the manufacture of cement, but a small amount of material of this nature could successfully be employed for recomposing the ordinary clay or shale base.

It is not improbable that highly siliceous materials similar to those in Romblon occur along tectonic lines and if so, then possibly a similar schist more available to Cebu, might be found on some of the smaller islands lying nearer to it. In fact, schists have been found on Cebu itself. These occur and outcrop only in a few places along the *Cordillera* under the capping. One such schist has been described as rhyolite by H. G. Ferguson.²²

Analyses of these materials rich in silica are given in Table VIII.

Sample No. 8. Sandstone which outcrops above the coal at the Compostela mine.

Sample No. 9. Average of two analyses, agreeing fairly well, of independent samples taken from the schist formation near Romblon, Romblon.

Sample No. 10. Cebu rhyolite.

TABLE VIII.—*Analyses of materials rich in silica.*

[The numbers give percentages.]

Constituent.	8.	9.	10.
Silica (SiO ₂)	72.76	80.12	67.25
Alumina (Al ₂ O ₃) ^a	15.58	12.56	13.12
Iron oxide (Fe ₂ O ₃) ^b	1.42	1.15	0.24
Lime (CaO)	0.62	0.12	1.23
Magnesia (MgO)	Trace.	0.48	1.10
Potash (K ₂ O)		2.88	4.38
Soda (Na ₂ O)		1.31	0.59
Loss on ignition	3.53	1.94	6.11
Water (H ₂ O) below 110°C.	1.84	0.21	6.15

^a Includes possible titanium oxide (TiO₂).

^b Total iron determined as ferric oxide.

²² *This Journal*, Sec. A. (1907), 2, 408.

Suppose that we recompose clay number 1 with schist number 9 so that, $\frac{\text{alumina (resp. iron oxide)}}{\text{silica}} = \frac{1}{3}$. The calculation is as follows:

Clay number 1.— $22.65 + \left(4.66 \times \frac{102.2}{159.8}\right) = 25.63$ parts alumina equivalent to alumina and iron oxide in 100 parts clay.
 $\frac{60.17}{25.63} = 2.346$ or $\frac{\text{silica}}{\text{alumina}} = 2.346$.

Schist number 9.— $12.56 + \left(1.15 \times \frac{102.2}{159.8}\right) = 13.30$ parts alumina equivalent to alumina and iron oxide in 100 parts schist.
 $\frac{80.12}{13.30} = 6.025$ or $\frac{\text{silica}}{\text{alumina}} = 6.025$.

For any given intermediate ratio, parts of each must be combined, inversely in proportion as the found ratio varies from that given. For a ratio of 3 to 1 therefore, 0.654 (*i. e.*, 3—2.346) part of schist would need to be combined with 3.025 (*i. e.*, 6.025—3) parts of clay, or a mixture of 82.25 per cent $\left(\frac{3.025}{3.025+0.654}\right)$ clay number 1 and 17.75 per cent $\left(\frac{0.654}{3.025+0.654}\right)$ schist number 9 would be required.

Accordingly, a new siliceous material would be obtained as follows:

TABLE IX.

[The numbers give parts of the materials by weight.]

Material.	Individual constituents.					
	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Loss on ignition.
82.25 clay (No. 1)-----	49.50	18.62	3.84	0.26	1.52	5.23
17.75 schist (No. 9) -----	14.23	2.23	0.20	0.02	0.09	0.38
100-----	63.73	20.85	4.04	0.28	1.61	5.61

The formula requires 3.475 parts of limestone number 7 to every part of the above material to give the maximum of lime which should be present in the cement mixture as follows:

TABLE X.

[The numbers give parts of the materials by weight.]

	Total.	Individual constituents.					
		Silica (SiO ₂).	Alu- mina (Al ₂ O ₃)	Iron oxide (Fe ₂ O ₃).	Cal- cium oxide (CaO).	Magne- sia (MgO).	Volatile (CO ₂ , H ₂ O+, etc.)
Clay (No. 1) -----	82.25	49.50	18.62	3.84	0.26	1.52	5.23
Schist (No. 9) -----	17.75	14.23	2.23	0.20	0.02	0.09	0.38
Limestone (No. 7)----	347.50	1.32	0.62	-----	193.50	-----	152.00
Unburned -----	447.50	65.05	21.47	4.04	193.8	1.61	157.6
Volatile -----	157.6						
Burned -----	289.9	22.48	7.40	1.39	66.8	0.55	-----

In ordinary practice this material would probably be combined with not more than 3 parts of limestone number 7 as follows:

TABLE XI.

	Total.	Individual constituents.					Volatile (CO ₂ + H ₂ O+, etc.)
		Silica (SiO ₂).	Alu- mina (Al ₂ O ₃).	Iron oxide (Fe ₂ O ₃).	Cal- cium oxide (CaO).	Magne- sia (MgO).	
Clay (No. 1) -----	82.25	49.50	18.62	3.84	0.26	1.52	5.23
Schist (No. 9) -----	17.75	14.23	2.23	0.20	0.02	0.09	0.38
Limestone (No. 7) ---	300.	1.14	0.54	-----	166.86	-----	131.
Unburned -----	400.	64.87	21.39	4.04	167.16	1.61	136.6
Volatile -----	136.6						
Burned -----	263.4	24.62	8.12	1.53	63.46	0.61	-----

In like manner the materials numbered 2 to 6 inclusive could be mixed with schist number 9 and limestone number 7. The following proportions would give a correction of the silica-alumina ratio to 3 to 1.

Sample number.	Parts sample.	Parts schist.
2	66.3	33.7
3	71.3	28.7
4	73.5	26.5
5	74.4	25.6
6	92.1	7.9

The composition of the ash of the coal has not been considered in preparing the above figures, but the relative proportions of the raw constituents may be varied to include this factor, which is not a large one.

It is not only the existence in this region of a superabundance of limestone and of shales that could readily be recomposed to be suitable for the manufacture of cement which attracts attention, but the coal is at hand; the city of Cebu is an open port making transportation easy and the cost of labor and supplies should be as low as they would be at any other point in the Islands.

FUEL FOR BURNING CEMENT.

The item of fuel used in the burning of Portland cement is an important one. In 1885 Mr. F. Ransome²³ patented a rotary kiln for calcining cement in which the firing was effected by means of producer-gas. The powdered raw material was fed in by means of a hopper at the upper end of the kiln and traveled slowly down the furnace in consequence of an angle of inclination and a constant revolution of the kiln, while the producer gas in a large volume of flame entered the kiln at the opposite end. The interior of the cylinder contained a series of projecting longitudinal steps by which the raw material was caught

²³ Redgrave, G. R. and Spackman, C., *Calcareous Cements* London (1905), 167.

up and carried until it would fall almost directly across the flame to the bottom, to be carried up again. It was found that the finely divided cement material was carried by the draft completely out of the kiln, and that it had to be intercepted at the exit end and returned to the feeding hopper. The use of producer-gas, without a regenerator (an apparatus for preheating the air to be mixed with the gas) failed to yield the requisite, steady temperature for the process of calcination, and when a regenerator using the waste gases was added, it speedily became clogged with the cement powder carried into it by the draft. Later inventors have overcome the greater portion of the difficulties and the mechanical defects of Ransome's apparatus have been removed by modifications and improvements, but the consumption of producer-gas does not seem as yet to have been brought to such a state of perfection that it competes with coal as a fuel for firing cement kilns. Both oil and natural gas have been and are still used as fuels.

The chief combustible for firing cement kilns is powdered coal, although ordinary gas coke has been used to a considerable extent. The class of coal to be employed is of special importance. Bituminous coal has been found to be most suitable. It must contain the proper quantity of volatile combustible matter to render it easy of ignition at the proper height in the cylinder in order to produce the maximum temperature at the right point. Anthracite and coke are more difficult to ignite, and therefore this maximum, when the latter are employed, occurs higher in the cylinder; the result is increased difficulty in watching the vitrification of the clinker and a less even distribution of the heat throughout the length of the cylinder.

The coal must be thoroughly dried, usually by rotary driers heated by hot air from the clinker coolers, before it can be ground to a sufficient degree of fineness. Care must be exercised in this operation that the temperature does not rise sufficiently to expel volatile combustible constituents of the coal.

The estimated coal consumption, based on the barrel as a unit, varies as much as from 30 to 100 kilograms because so many factors enter into the calculator. Theoretically, the amount of fuel needed in the kiln must be sufficient to expel any moisture, to drive off the carbon dioxide from the calcium carbonate and to produce the chemical combination of the silica and lime, and the silica and alumina; practically the amount is much larger than that required by theory because the ordinary rotary kiln has never been made to work economically. The calorific value of the coal, the burning temperature required, the heat lost by the radiation from the kiln walls, by the discharge of the hot clinker and the escaping gases, the completeness of combustion of the fuel, the excess of air supply, the moisture in the raw materials and the experience of

the burner must all be considered. The consumption of fuel is much greater with slurry, which usually enters the kiln with 50 per cent of water, than with dry flour, while the output is less.

Richards²⁴ has worked out a balance sheet of the heat generated within and the distribution of the heat of a rotary cement burner, 60 feet long by 6 feet external diameter, fired by pulverized bituminous slack, at the plant of the Dexter Cement Company at Nazareth, Pennsylvania. The coal, which was from Fairmont, West Virginia, and which required 50 kilograms per barrel, gave the following analysis:

Constituent.	Per cent.
Moisture	0.60
Volatile combustible matter	38.10
Fixed carbon	53.24
Ash	8.06
Total	100
Calories (calculated)	7,900

The average results were 1,650 kilograms of clinker with 90 kilograms of flue dust per hour from 2,710 kilograms of mixture fed to the kiln. The temperature of the clinker falling out of the lower end of the kiln was 1,200° and the temperature of waste gases in the chimney about 1 meter from the upper end of the kiln was 820°. The following table gives a summary of the results obtained by Richardson.

TABLE XII.

The ground cement mixture from which the carbon dioxide and water had to be expelled.		The burnt cement clinker (per cent).	The waste gases.	
Constituent.	Per cent.		Constituent.	Per cent.
Silica	13.38	21.27	Carbon dioxide	10.2
Aluminium oxide	6.04	6.42	Oxygen	11.8
Ferric oxide		3.18	Carbon monoxide	0.2
Calcium oxide	41.96	66.70	Sulphur dioxide	(*)
Magnesium oxide	1.53	2.43	Water	(*)
Carbon dioxide	34.65		Nitrogen	(*)
Water	0.43			

* Undetermined.

The items and results of the investigation are shown by the following table, based on the consumption of 100 kilograms of coal, or the production of 2 barrels of cement.

Heat generated.

	Calories.
(1) Theoretical heating power of the fuel	790,000
(2) Heat of combination of the ingredients forming clinker	142,819
Total	932,819

²⁴ Richards, J. W.: *Journ. Am. Chem. Soc.* (1904), 26, 80.

Heat distributed.

	Calories.	Percentage of the whole.
(1) Heat in the clinker	100,050	10.7
(2) Heat in the chimney gases:		
(a) In the excess air admitted	336,000	36.0
(b) In the necessary products	340,000	36.5
(3) Heat in flue dust	2,112	0.2
(4) Lost by imperfect combustion	12,248	1.3
(5) Evaporation of water of charge	1,446	0.2
(6) Expulsion of carbon dioxide from carbonates	21,628	2.3
(7) Loss by radiation and conduction	119,335	12.8
Total	932,819	100.0

Richards calls attention to the fact that the maximum temperature to which the 790,000 calories (the available heat of combustion) will heat the gases is 1,000°, while the clinker leaves the kiln at 1,200°. The difference is due to the heat of combustion of the mixture. In the zone of highest temperature the clinker is unquestionably heated much more than 200° above the estimated flame temperature, for the heat of reaction, which is equal to 15 per cent of all the heat developed, is generated in this region; furthermore Campbell²⁵ has shown that "the minimum temperature necessary to produce Portland cement which will give a perfect pat test from fresh clinker is about 1,450° C. This temperature is for a minimum amount of calcium oxide. It increases with increase of calcium oxide until in ordinary commercial cements it reaches 1,550°. It depends somewhat on the length of time required to pass through the rotary, slow driving tending to lower the temperature."

EXPERIMENTAL.

It is of especial importance that an examination of available Philippine coals from the point of view of their usefulness as a fuel for cement burning be undertaken. A few results are given in Table XIII.

²⁵ Campbell, E. D.: *Journ. Am. Chem. Soc.* (1902), 24, 991.

TABLE XIII.—Analyses of some available Philippine coals and of some foreign coals.

	Philippine coals.					Foreign coals.	
	Camansi (vein No. 2) near Danao, Cebu.	Camansi (general picked sample).	Military Reservation, Batan Island.	Betts', Batan Island.	Polillo.	Australia. ^a	Fairmont, West Virginia, gas coal. ^b
Moisture	11.28	11.02	5.87	18.61	5.89	2.80	1.34
Volatile combustible matter	38.20	38.24	38.99	36.50	39.29	34.23	35.88
Fixed carbon	46.76	48.05	50.30	34.86	48.82	50.94	54.03
Ash ^c	1.03	0.67	1.40	4.70	3.00	6.81	3.59
	Silica (SiO ₂)						
	Alumina ^d (Al ₂ O ₃)	0.85	1.28	0.78	1.08	3.64	3.58
	Iron oxide (Fe ₂ O ₃)	0.71	0.60	1.31	0.58	0.92	
	Lime (CaO)	0.47	0.40	1.06	0.82	0.82	0.75
	Magnesia (MgO)	0.13	0.08	0.54	0.22	0.14	0.03
	Soda (Na ₂ O)	0.04	0.03	0.05	0.04	0.11	0.10
	Potash (K ₂ O)	0.01	0.01	0.02	0.04	0.09	0.16
	Sulphuric anhydride (SO ₃)	0.01	0.05	0.08	1.53	0.00	0.54
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Sulphur (separately determined)	0.38		0.09	1.21		0.09	1.77
Calorific value (calories)	6,230	6,264	6,359	4,560	6,285	6,614	

^a This coal was purchased by the Insular Government at ₱10.75 per ton of 2,240 pounds, piled in its sheds and yards. Coal of this class is available on the Manila market.

^b *The Chem. Eng.* (1905), 2, 223.

^c Manganese and phosphoric anhydride were present in traces or not at all.

^d Includes titanic oxide (TiO₂).

I am indebted to Mr. L. A. Salinger of this laboratory for his assistance in making these analyses.

DISCUSSION.

Meade²⁶ has shown by three experiments that the changes between the clinker as analyzed, when calculated without its water and carbon dioxide, and the raw material calculated to a clinker are as follows:

TABLE XIV.—*Loss or gain.*

[The numbers give percentages.]

Constituent.	1.	2.	3.	Average.
SiO ₂ -----	+0.46	+0.72	+0.67	+0.62
TiO ₂ -----	-0.02	0.03	-0.03	-0.03
Al ₂ O ₃ -----	+0.41	+0.32	+0.39	+0.37
Fe ₂ O ₃ -----	+0.26	+0.30	+0.32	+0.29
FeO -----	-All.	All.	All.	-----
MnO -----	-0.01	-----	0.00	0.00
CaO -----	0.20	-0.09	+0.08	0.00
MgO -----	+0.05	0.08	0.03	0.00
Na ₂ O -----	-0.06	-0.12	-0.09	-0.09
K ₂ O -----	-0.44	-0.51	-0.51	-0.49
P ₂ O ₅ -----	-0.02	+0.01	-0.00	0.00
SO ₃ -----	-0.43	-0.72	-0.87	-0.67

The results show that there is almost complete oxidation of the iron present in the raw state, that over one-half of the alkalis are expelled in the kiln, and especially that there is a large loss of sulphur and almost complete oxidation of the remainder. The greater part of the sulphur is present as iron sulphide in the coal and the original rock which, when heated to the temperature of the kiln, burns to sulphur dioxide and ferric oxide. It is quite probable that in the coal ash as obtained in the laboratory all of the sulphur is fixed by being roasted to sulphates which do not give off sulphuric anhydride at a gentle heat. At kiln temperatures sulphuric anhydride would be partially expelled from these and for this reason we would expect a loss of sulphur. As regards sulphur, then, even the Philippine coals containing the highest percentage that I have found would be available for burning cement.

Meade shows that the silica, ferric oxide and alumina of the clinker have been increased by approximately one-half of the coal ash. On the other hand, he finds a marked loss of material in the dust, which the analyses indicates to be a mixture of coal ash, partially burned raw material and the volatile constituents of the latter. The figures show that theoretically 254 kilos of rock should make a barrel of cement (172 kilos), but that few manufacturers use less than 276 kilos, showing a loss of 12 kilos as dust, etc., per barrel of cement produced. Mr. Meade further says:

"Undoubtedly in the rotary kiln much of the ash is carried out with the gases by the strong draft of the kiln. This we would expect to be the case when we

²⁶ *Chem. Eng.* (1905), 2, 222-223.

consider that the particles of ash are of the same volume as the particles of coal, and yet only one-tenth their weight, for when the coal burns it leaves its ash in the form of a skeleton. These particles of ash are already in motion and are in the full draft. The gases have a velocity of at least 600 meters per minute, which is quite sufficient to carry the particles up the chimney. It seems probable in view of these facts that what ash does contaminate the clinker comes from the impinging of the flame upon the material in the kiln."

The sulphur content in nearly all of the Philippine coals which have been analyzed by the Bureau of Science would not be injurious were it accepted as a fact that all of it is absorbed by the cement clinker. The other constituents of the ash may be incorporated into the cement clinker by proper fluxing. When one-half of these are lost to the stack, the additional amount of raw material which must be added is small. It is probable that if the coal is ground to a sufficient degree of fineness the ash particles will be almost entirely swept out of the kiln by the draft and the factor of the ash will become very small.

There remains the question of the heating value of the coal. The average of 51 samples of Fairmont coal ²⁷ which has been considered above as a fuel for burning cement, shows the following analysis and calorific value:

Water	1.43
Volatile combustible matter	37.47
Fixed carbon	53.83
Ash	7.27
Sulphur	2.59
Calories	7,785

This analysis, which represents a vast territory and perhaps the best American fuel for cement kilns, when calculated to the dry coal would have a calorific value of about 7,900 calories. Other coals of less calorific value have been satisfactorily used as a fuel for burning cement. The Philippine coals, the analyses of which are given in the table on page 227 when calculated to the dry coal would have a calorific value of about 7,090, 7,110, 6,800, 5,715 and 6,715, respectively, while that of the Australian coal would be 6,775 calories. While the fuel value of the Philippine coals is not as great as the well-known gas coal of Fairmont, West Virginia, our coals appear to be as good under these conditions as any at present available in the Philippines and neighboring countries and I am of the opinion that they will be very useful as a fuel for burning cement.

²⁷ *Report of the Geol. Sur. W. Va.* (1903), 2, 231.

EDITORIAL.

PHILIPPINE TURPENTINE.

Considerable local interest has been aroused recently in the industrial possibilities of turpentine products from the pine forests of Benguet Province, Luzon.

The Benguet pine, "Saleng," *Pinus insularis* Endl., is found distributed from Zambales Province to the extreme north end of Luzon. The Bureau of Science herbarium shows collections of this species from the Provinces of Zambales, Benguet, Ilocos Sur, Abra, Lepanto, and Bontoc.

The tree, in its leaf, fruit, and wood characters, shows a close resemblance to the western yellow pine, *Pinus ponderosa* Dougl., of the United States and to the Khasya pine, *Pinus khasya* Royle, of British India. Neither of the above-mentioned species to my knowledge are tapped for the commercial production of turpentine at the present time, although the latter is reported to produce a good grade of resin.

Some Benguet pine trees were boxed and the turpentine collected by Mr. B. T. Brooks of the chemical staff of the Bureau of Science, who reported in substance as follows:

"On March 13, fourteen trees situated in the forest adjoining the claim of the Headwaters Mining Company were boxed. The trees were selected at random and included several trees of the variety known to lumbermen and turpentine collectors as 'scrub pine.' Six hours later thirteen of the trees showed an abundant flow of resin, while one was hard and did not flow. The collected resin weighed 1,761.5 grams.

"On March 14, thirty trees were boxed in another locality about 2 miles distant from Baguio. They were selected with the idea of including both healthy and unhealthy looking trees and some which had been damaged by ground fires. On the following day these trees were again visited and all but three, which were hard and did not flow, were still running slowly. The collected resin weighed 4,400 grams.

"*Method of boxing.*—The boxes were cut about 30 to 40 centimeters wide, 12 to 18 centimeters deep, and 6 to 8 centimeters from front to back, varying with the size of the trees. They were made by inexperienced laborers and were so badly split and bruised that much of the fresh resin was lost, hence the yields obtained do not accurately represent the total flow of resin.

"One of the best flowing trees had a diameter of about 85 centimeters and produced 857 grams of resin in thirty-two hours, although a portion was lost by overflowing the box.

"These samples being taken during the dry season probably represent a smaller yield than would be obtained during the rainy season when the trees have more life and the loss by evaporation is less.

"The cup and gutter system of collection would also give large yields by minimizing the loss."

A sample of the crude turpentine collected under the above conditions was submitted for an examination and for an opinion as to its commercial value. It had much the appearance and consistency of crystallized honey and possessed a mild, pleasant odor. 1,961.5 grams were subjected to steam distillation as received without any previous filtering for the removal of an appreciable quantity of foreign matter in the form of chips, bark, etc. Exhaustive distillation gave 412.2 grams (23.4 per cent) of oil of turpentine which was water-white in color and after drying over calcium chloride it possessed the following constants: Specific gravity, $\frac{30^\circ}{30^\circ}=0.8593$; $N \frac{30^\circ}{D}=1.4656$; $A \frac{30^\circ}{D}=+26.5$. Ninety-six per cent distilled between 154° and $165^\circ.5$ C.

The residue from the steam distillation, amounting to 76.6 per cent of the original resin by difference, was freed from approximately 15 grams of foreign material by hot filtration. It consisted of prime colophony of a clear, pale amber color.

GEORGE F. RICHMOND.

INDUSTRIAL ALCOHOL AND ITS POSSIBILITY AS A SOURCE OF POWER IN THE PHILIPPINES.

Alcohol can be used as a motor fuel for all purposes for which gasoline is at present employed. Exhaustive tests made by the United States Government¹ have demonstrated that any gasoline or kerosene engine of ordinary type can with proper manipulation operate with alcohol without material change in its construction. The engine will give slightly more power (about 10 per cent) when alcohol is used but this increase is at the expense of greater consumption of fuel. Experiments of the United States Geological Survey² have shown that when denatured alcohol is employed the lowest fuel consumption is obtained with the highest practical degree of compression (11.6 to 13.7 kilograms per square centimeter), but since the vaporization temperature of alcohol is higher than that of gasoline a modified combustion chamber and carburetor is to be preferred. Some gasoline engines are not sufficiently heavy to stand the desired high explosion pressure when alcohol is used and therefore a machine especially designed for alcohol is preferable to one planned to operate with gasoline or kerosene.

The United States Geological Survey made a series of over 2,000 individual tests, comparing gasoline of about 0.699 specific gravity (73° Baumé) and commercial fully denatured alcohol.³ Tests which corre-

¹ Lucke, C. E. and Woodward, S. M.: *Farm. Bull. U. S. Dept. Agr.* (1907), 277; Holmes, J. A.: *Eng. News* (1908), 59, 424.

² Holmes, J. A.: *Ibid.*; C. A. (1908), 2, 2147.

³ Holmes, J. A.: *Ibid.*

sponded in the method of manipulation showed that alcohol was more efficient than gasoline and they also proved that equal volumes of gasoline and alcohol produced about the same power. This result is not usually achieved in practice. Ordinary commercial gasoline engines of stationary or marine type will consume from 1.5 to 2 times as much alcohol as gasoline when operated under the same conditions.

Alcohol is especially suited to air-cooled automobile engines, as the exhaust is not so hot as when gasoline or kerosene is used, while on the other hand the temperature of the cylinder may be hotter without danger of backfiring. The storage and use of alcohol in engines is much less dangerous than that of gasoline or petrol and the engines operating on the former run more quietly and produce a less offensive odor. No more skill is required to operate an alcohol engine than one arranged for gasoline or kerosene.

The relative heat values of gasoline, alcohol and coal are shown by the following approximate numbers:

	Calories.
Gasoline	11,100
Alcohol (100 per cent)	7,183
Pennsylvania anthracite	7,500

The calorific value of alcohol is of course lower by impurities, so that commercial (90 per cent) alcohol has a calorific value of about 60 per cent of that of gasoline, or a comparative heat value of over 70 per cent by volume. Alcohol of 85 per cent is the common grade of industrial alcohol used in Europe. The United States Geological Survey found difficulties in starting and regulating when the experimenters employed 80 per cent alcohol and the fuel consumption increased more rapidly than the percentage of alcohol decreased.

The effect upon motors, lamps, etc., of using denatured alcohol has been discussed and deterioration has usually been attributed to the denaturant.⁴ It may be possible that all of the evils coming from the latter may be remedied in the future. Lucke and Woodward found that the interior of an alcohol engine had no tendency to become sooty, as is the case with gasoline and kerosene and there was no undue corrosion of the interior due to the use of alcohol.

The raw materials from which industrial alcohol comes consist of those substances which contain starch, sugar and other fermentable bodies, named in the order of their importance, capable of easily being converted into a fermentable sugar. The cereals, rice, wheat, oats, rye, maize and barley, the potato, cassava or manioc and some other roots contain large percentages of starch. From all of these as well as from sugar cane and sugar-cane molasses, sorghum and fruit juices which contain large percentages of sugars, alcohol is made. The artichoke

⁴ Suchemin, R.: *Rev. gén. chim.* (1906), 9, 437 to 443; Lucke, C. E. and Woodward, S. M.: *loc. cit.*

which contains neither starch nor sugar but a number of other fermentable carbohydrates of which inulin and levulin are the principal constituents has been highly recommended and rather extensively used in Germany for the manufacture of alcohol.⁵ At the present time alcohol is made on a large commercial scale from corn, rye, potatoes, sugar beets, sugar cane, and sugar-cane molasses. Rice has the largest percentage of starch among the cereals, but it is not the cheapest source of alcohol. Indian corn, which hitherto has formed the chief raw material for fermentation and distillation, contains approximately 70 per cent of fermentable bodies and under the best conditions a kilo of corn will usually yield about 340 grams of alcohol (420 cubic centimeters of 95 per cent alcohol by volume at 15° C.). If the average price of corn be placed at 3 centavos per kilo and the cost of manufacture, storage, profit, etc., be taken as an equal amount, industrial alcohol (95 per cent) from this source, untaxed, would sell wholesale for about 14 centavos a liter.⁶

	Retail price per liter, in centavos.	Annual consumption (million liters).
Germany	16	140
Cuba	21	
France	23	40
England		15
United States	32	13

Besides rice, Indian corn, and sugar cane, the available sources from which alcohol can be manufactured in this Archipelago are the sap of many palms and the cassava. At present nearly all of the alcohol produced comes from the bled sap of the nipa and other palms.⁷ Alcohol from the nipa has a disagreeable odor which is somewhat difficult to remove, but for industrial purposes this would be of no consequence. A description of this palm (*Nipa fruticans* Wurmb.) may be found in many places.⁸ It is a species widely distributed all the way from India to Malaya, in northern Australia and Polynesia. A very detailed study of the culture and bleeding of this palm has been published by Ayala & Co.⁹

The nipa grows in low, salt-water tidal swamps and the plant is completely developed in about four years after planting the seed. The palms, fruit about every two years, at no particular season. When the tree is ready to bleed, the

⁵ Wiley, H. W.: *Farm. Bull. U. S. Dept. Agr.* (1906), 268, 14.

⁶ The following retail prices and annual consumption of denatured alcohol (approximately 95 per cent) are calculated from data given by R. F. Herrick (*Technol. Quart.* (1908), 21, 7 to 9):

⁷ During the fiscal year 1907-8, the figures of the Bureau of Internal Revenue show that the production from all sources was equivalent to about 4½ million liters of 95 per cent alcohol. There were practically no exports.

⁸ Hooker, *Fl. Brit. Ind.* (1892), 6, 424; Blanco, *Fl. Filip.* (1837), 662; Ed. 2 (1845), 461.

⁹ Conrado, A., and Zobel, E., *Estudio de la Planta Nipa*, Manila (1906).

fruiting stem is cut as close to the young fruit as possible and the emerging liquid (*tuba*) caught in a joint of bamboo. Every day a very thin slice is cut from the stem to prevent the pores from becoming clogged. The removal of thick slices will destroy the stem before all the *tuba* can be drawn.

The production of *tuba* from a mature tree usually increases during the first fifty to sixty days after tapping and decreases during twenty-five to thirty days more. If *tuba* is drawn for a longer period the tree will die. The *tuba* from mature stems is white, has an aromatic odor and is sweet. That from palms having less mature fruit is bluish and less sweet and, therefore, has less fermentative value. The average yield per tree fluctuates from one-half to 3 liters per day, with a total of from 30 to 40 liters (sp. gr. 1.07 to 1.08 at 15°. The juice contains approximately 12 per cent of fermentable material which is largely saccharose. Thirty-two to 34 liters of *tuba* will usually produce one liter of pure alcohol. In the Provinces of Bulacan and Pampanga, where the price of the molasses residues from sugar cane is low, the latter is mixed with the *tuba* before fermentation and is said to give a larger yield of alcohol than would the two if fermented separately.

Alcohol is removed from the fermented *tuba* by distillation. The method used in the provinces produces a distillate containing about 50 per cent of alcohol. By redistilling a sufficient number of times a 95 per cent alcohol might be produced, but the process would be very expensive; therefore, the crude alcohol is shipped to the large distilleries in Manila, where it can be refined more economically. In the latter, the process is continuous; the vapors pass through several stills and are cooled just sufficiently to condense them in each one until the proper purity is reached. It will, therefore, be seen that after an alcohol once passes the crude 50 per cent stage a purity of 95 per cent can be produced with very little more expense per proof liter than one of lower grade. The economy of the purer form is obvious.

The manufacture of alcohol from *tuba* is rather expensive and it is doubtful if the process could be greatly cheapened. Denatured alcohol (95 per cent) from this source is sold wholesale at 2.40 pesos, Philippine currency (1.20 dollars, United States currency) per 15 liters, while the above estimated price for the product from corn would be 2.30 pesos per 15 liters. If a market for alcohol as a fuel were opened it could undoubtedly be produced from *tuba* for 2 pesos per 15 liters, but with the present spasmodic usage it can not be sold at that figure.

Cassava is grown in the United States over a large area of the South Atlantic and Gulf States and numerous analyses made by the Division of Chemistry, United States Department of Agriculture¹⁰ have shown that the roots contain about 30 per cent of starch. With the exception of cereals it contains the largest amount of fermentable matter.

"An average crop of cassava in the United States may be placed at 5 tons of roots per acre on the ordinary lands of Florida, with proper preparation and

¹⁰ *Farm. Bull. U. S. Dept. Agr.* (1903), 167, 23; 268, 17; *Bull. U. S. Dept. Agr. Div. of Chem.* (1900), 58, 36.

cultivation and appropriate fertilization, a yield of from 4 to 7 or perhaps 8 tons per acre may be reasonably expected."¹¹ At present there are no reliable figures on the amount that can be produced on a given area of land in the Philippines. R. F. Bacon,¹² thinks that it is perfectly safe to figure on a production of 22½ metric tons per hectare (10 tons per acre). "With this yield," he says, "there is only one other substance which seems able to compete with it as a source of alcohol, namely, the molasses residue from the crystallization of cane sugar." E. B. Copeland,¹³ estimates that when starch made from cassava sells at its present local price (15 centavos per kilo), alcohol from the same source would be worth about 17½ centavos per liter or 2.60 pesos per 15 liters.

At present prices, it would be more profitable to produce starch than alcohol at a price below the latter figure. If at any time the production of cassava becomes more abundant and the utilization for other purposes less remunerative, alcohol from this source may be placed on the market very cheaply.

Some experiments with alcohol were carried out in Manila a few months ago with the 25-horsepower motor road roller purchased by the city of Manila. In all cases the machine was operated on a level road and at a standard speed. A crude alcohol such as is shipped to Manila by provincial distillers was used. The motor was first heated to a slight extent by being run for about ten minutes with gasoline; it ran for twelve minutes on the alcohol and then stopped. An examination showed that the explosions of the alcohol did not furnish enough heat to evaporate all of the water present and that a quantity had collected in the combustion chamber. When 90 and 94.5 per cent alcohol were employed the motor ran smoothly, with a consumption of 1.8 and 1.6 times, respectively, the quantity of gasoline used for the same time. Lucke and Woodward¹⁴ say that a small engine required 1.8 times as much alcohol (probably 85 per cent) as gasoline per horsepower hour.

The utilization of alcohol as a fuel is an established fact. The economy is the only open question. Gasoline (73°) is now sold in Manila at 2.38 pesos per 15 liters (about 16 centavos per liter). On the basis of an engine consuming 1.5 times as much 95 per cent alcohol as gasoline the former would need to be sold at 1.60 pesos per 15 liters in order to compete with the latter. In localities where alcohol can be produced cheaply and which are remote from gasoline supply, alcohol may immediately compete with gasoline as a power fuel, otherwise it is not probable that it will be as economical a fuel as gasoline in these Islands for some time to come and I do not anticipate an immediate change in our motor fuel.

ALVIN J. COX.

¹¹ *Bull. U. S. Dept. Agr. Div. Chem.* (1900), 58, 36, 42.

¹² *This Journ. Sec. A.* (1907), 2, 93.

¹³ *Phil. Agr. Rev.* (1908), 1, 145.

¹⁴ *Loc. cit.*, 39.